CHEMICAL ENGINEERING TRANSACTIONS
VOL. 59, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216

DOI: 10.3303/CET1759047

Rheological Properties of Steam-Exploded Corn Straw Slurry and Enzyme Hydrolysate

Xia Zhang[a*], Hongwei Li[b], Xiaohang Feng[c]

[a]Institute of Environmental & Municipal Engineering, North China University of Water Resources Electric Power, Zhengzhou, 450001, China
[b]Zhejiang Runtu Company Limited, Shangyu 312300, China
[c]School of Foreign Languages,Peking University, Beijing 100871, China
1732740949@qq.com

In order to reveal the rheological properties of corn straw slurry and enzyme hydrolysate, this paper employs rotary viscometer, pre-treats the corn straw via steam explosion, and examines the slurry rheological behavior based on insoluble substrate concentration. The results are shown that the corn straw slurry exhibits shear-thinning, the power law model is suitable to describe the behaviors for corn straw slurry, and the regression coefficients exceed 0.98 in all cases. The apparent viscosity decreases with the increase in temperature, the data of experiment for that is described by Arrhenius equation with regression coefficients exceeding 0.94 at different substrate concentrations. And then the apparent viscosity grows with the solid concentration, which is accompanied by a decrease in the amount of free water. The time-dependent characteristic for corn straw slurry is obvious at different shear rates due to fiber suspension. The sugar concentration of enzyme hydrolysate rises at different substrate concentrations, and the apparent viscosity keeps falling throughout the enzyme hydrolysis process.

1. Introduction

The enzyme hydrolysis process of steam-exploded corn straw involves a polyphase biochemical reaction which takes place with constant temperature and a fully-dispersed matrix. To design an enzyme hydrolysis operation unit and reactor, it is of great necessity to learn about the rheological properties.

Previous researches had been done on the rheological properties of corn straw suspension pretreated by acid and enzyme hydrolysis. For instance, Natalia and Thomas (2003 and 2004) explored the rheological properties of acidized corn straw suspension at the substrate concentration between 5% and 30%, and suggested that the suspension belonged to the non-Newtonian fluid and had a yield stress consistent with the Herschel-Bulkley model. Sridhar et al., (2009) studied the rheological properties of acidized corn straw suspension with high solid content (10%~40%), pointing out that the suspension borne shear-thinning characteristics, and that the apparent viscosity and yield stress were impacted by solid content. Probing into the hydrolysis process of corn straw pretreated by acid, Ehrhardt et al., (2010) argued that the apparent viscosity increased with solid content, but reduced with the rise of hydrolysis temperature and acid dosage. Taking acidized corn straw as the raw material, Kyle et al., (2010) examined the viscosity variation of enzyme hydrolysate, and concluded that the enzyme hydrolysate exhibited the properties of Newtonian pseudo-plastic fluid and conformed to the power law model. Literatures (Mustafa, 2011; Mat and Guido, 2007) revealed that the acid pretreatment could catalyze and decompose hemicellulose, and the steam explosion pretreatment only degraded part of cellulose and lignin; through the pretreatments, the cellulose was fully exposed but the hemicellulose and lignin were not completely removed (Mustafa, 2011; Mat and Guido, 2007). The raw materials processed by the two different pretreatment methods carried different physicochemical properties. Despite the above research, there has not been any report on the rheological properties of steam-exploded corn straw suspension and enzyme hydrolysis.

Please cite this article as: Xia Zhang, Hongwei Li, Xiaohang Feng, 2017, Rheological properties of steam-exploded corn straw slurry and enzyme hydrolysate, Chemical Engineering Transactions, 59, 277-282 DOI:10.3303/CET1759047

2. Experimental

2.1 Materials and methods

The cellulose enzyme and steam-exploded corn straw (cellulose content: 32.3%, hemicellulose content: 28.0%, lignin content: 29.2%,) are provided by Henan Tianguan Group Co., Ltd., and other reagents are analytically pure. The instruments and equipment include a 7L fermenter (Shanghai BaoXing Bio-Engineering Equipment Co., Ltd.), an NDJ-79 series rotary viscometer (Shanghai Sendi Scientific Instrument And Equipment Co., Ltd.), and a HH-601 super constant temperature water bath (Jiangsu Jintan Medical Instrument Plant).

2.2 Preparation of enzyme hydrolysate

The enzyme hydrolysate is prepared in the following steps: Dry the steam-exposed corn straw to constant weight at 103±2°C, and relocate a certain volume of the corn straw to the 7L fermenter according to the substrate concentration; add cellulose enzyme in the proportion of 60 IU/(g substrate); apply a certain volume of buffer (pH 4.8) to increase the total mass of suspension to 5,000g; maintain the temperature at 50.0 ±1.0°C, and the stirring speed at 300 r/min; take 100mL enzyme hydrolysate every time and measure the apparent viscosity of enzyme hydrolysate at different shear rates; extract another 10mL enzyme hydrolysate and relocate it into a centrifuge tube; take the supernatant fluid after the centrifugal process, and determine the content of reducing sugar.

2.3 Determination

The cellulase enzyme activity is measured by filter paper activity (FPA) method (Ghose, 1987).
The viscosity is measured by the NDJ-79 series rotary viscometer.
The glucose concentration is determined by the DNS method (Ghose, 1987].

3. Results and discussion

3.1 Steam-exploded corn straw slurry rheological properties

3.1.1 The relationship between the apparent viscosity of the suspense and the temperature
The temperature is a major influencing factor of the apparent viscosity. The experimental parameters are designed as follows: substrate concentration 5% (w/w), temperature 2~70°C. Figure 1 illustrates the variation in the apparent viscosity with temperature.

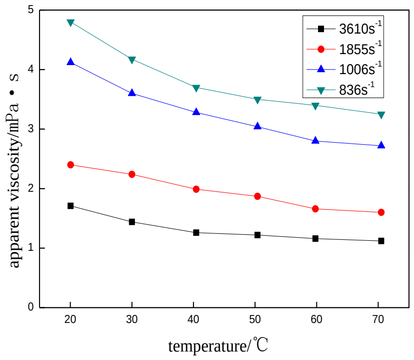

Figure 1: Influence of temperature on the apparent viscosity in different shearing rates

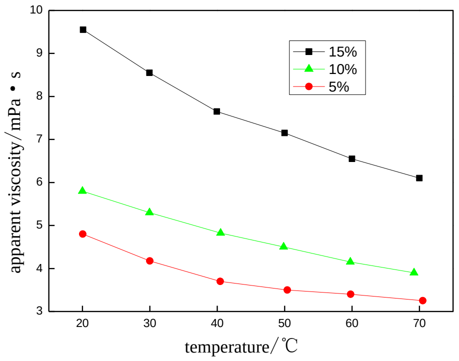

Figure 2: Influence of temperature on the apparent viscosity in different substrate concentrations

From Figure 1, it is learned that the apparent viscosity of steam-exploded corn straw suspension shows a downward trend as the temperature increases at different shear rates. When shear rate is 3,610 s^{-1}, the apparent viscosity of the suspension drops by about 41.36%. When the shear rate is 836 s^{-1}, there is a 34.50% decline in apparent viscosity. The steam-exposed corn straw suspension mainly consists of water. As the temperature rises, the resulting expansion of the fluid widens intermolecular distance, weakens molecular interactions among particles, decreases the resistance to molecular relative motion, and eventually causes significant reduction of apparent viscosity.

3.1.2 The relationship between slurry apparent viscosity and the temperature

The steam-exposed corn straw suspension falls into the category of fiber suspension. The nature and the apparent viscosity of the suspension are inevitably affected by the content of fibrous particles. The effect of temperature on apparent viscosity is measured at different substrate concentrations. The experimental parameters are designed as follows: substrate concentration 5%~15% (w/w), temperature 20~70°C, and the shear rate 836 s^{-1}. The results are shown in Figure 2.

It can be seen from the figure that: the slurry apparent viscosity also shows a downward trend as the temperature increases at different substrate concentrations. The decline range varies with the substrate concentration. As the temperature increases from 20°C to 70°C, the apparent viscosity is reduced by 32.29%, 32.76% and 36.13% respectively at the substrate concentrations of 5%, 10% and 15%.

Figure 2 also demonstrates that, under the same temperature, the apparent viscosity of the 15% substrate concentration suspension is the highest at the shear rate of 836 s^{-1}. The result is explained as follows: the increase of substrate concentration reduces the amount of free water among fibers and greatly enhances the interaction force among fibers. When the fibers are in direct contact with each other in the suspension, they could form a reticular structure because of different orientations. The complex structure contributes to the growing resistance to mutual movement, which, in turn, increases the apparent viscosity.

As the substrate concentration of the suspension continues to increase, more and more solid mesh structures form inside the suspension. In this case, it is not suitable to measure the apparent viscosity with rotary viscometer.

It is widely accepted that the temperature characteristics of fluid viscosity can be approximately described with the improved Arrhenius correlations under slight temperature fluctuations（Liu and Ma, 2003; Ren at al., 2007):

$$\eta_a = Ae^{\frac{B}{T}} \quad (1)$$

Where η_a is the apparent viscosity, MPa·s; T is the temperature, K; A and B are constants.

Formula 1 can be rewritten as:

$$\ln\eta_a = \frac{B}{T} + \ln A \quad (2)$$

Taking the T^{-1} as the x-axis and $\ln\eta_a$ as the y-axis, the author remaps the variation in the apparent viscosity with temperature at different substrate concentrations (Figure 3). The fitting results are shown in Table 1.

According to the fitting results, the R^2 is greater than 0.94, indicating that the Arrhenius-type relationship between viscosity and temperature applies to the steam-exposed corn straw suspension. The greater the value of B, the more the apparent viscosity is dependent on temperature [Yang et al., 2002]. It is also inferred from the table that: the value of B increases with the substrate concentration. Hence, the temperature-induced variation in apparent viscosity grows stronger with the increase in substrate concentration.

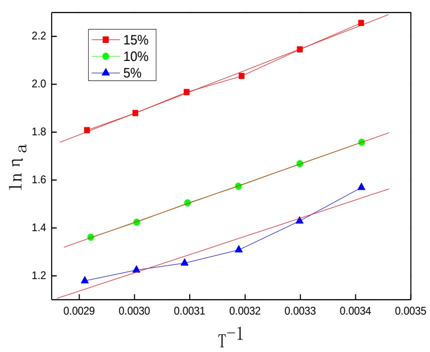

Figure 3: Relationships of lnη$_a$ & T^{-1}

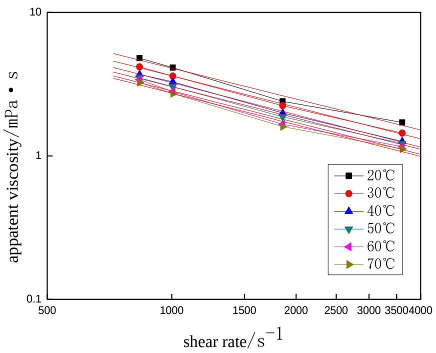

Figure 4: Relationships of apparent viscosity & shearing rate

Table 1: Fitting results of viscosity-temperature characteristics

Substrate concentration/% (mass)	A	B	R^2
5	0.3504	0.7469	0.9405
10	0.3708	0.7978	0.9997
15	0.4559	0.8801	0.9966

3.1.3 The relationship between suspension apparent viscosity and the shear rate

The addition of suspension inevitably changes the rheological properties. To disclose the relationship suspension apparent viscosity and shear rate, the experimental parameters are designed as follows: substrate concentration 5% (w/w), temperature 20~70°C, the shear rates: 836 s^{-1}, 1006 s^{-1}, 1855 s^{-1} and 3610 s^{-1}. The results are depicted in Figure 4. In light of Figure 4, the suspension apparent viscosity is negatively correlated with the shear rate, making the suspension a non-Newtonian pseudo-plastic fluid. Through the data analysis, the author concludes that the suspension conforms to the power law model.

The power law equation is expressed as:

$$\tau = K_{psu}|\dot{\gamma}|^{n-1}\dot{\gamma} \qquad (3)$$

Where τ is the shear stress, Pa; K_{psu} is the consistency coefficient, Pa· sn; n is the fluid rheological index, dimensionless; $\dot{\gamma}$ is the shear rate, s^{-1}.

The equation can be rewritten as:

$$\mu_a = K_{psu}|\dot{\gamma}|^{n-1} \qquad (4)$$

Where τ is the apparent viscosity, Pa·s.

The experimental data are fitted by Formula 4, and the results are shown in Table 2.

In Table 2, the rheological index n varies between 0.2538 and 0.2831. The range is so small that the index is nearly unchanged. Ranging between 0.4310 and 0.5786, the consistency coefficient decreases slightly with the temperature increase. The downward trend is resulted from the growing solution volume under the rising temperature. The R^2 is greater than 0.98, signifying that the experimental results are well matched with the power law equation. Thus, it is reasonable to believe that the suspension is a power law fluid.

Table 2: Fitting results with Power Law equation

Temperature/°C	*n*	K_{psu}/Pa·s^n	R^2
20	0.2831	0.5786	0.9831
30	0.2707	0.5576	0.9983
40	0.2538	0.5617	0.9984
50	0.2746	0.4558	0.9973
60	0.2652	0.4551	0.9839
70	0.2676	0.4310	0.9847

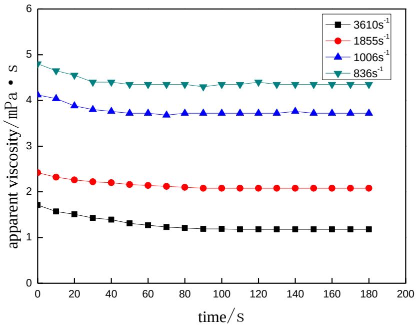

Figure 5: The time-dependent characteristic of apparent viscosity

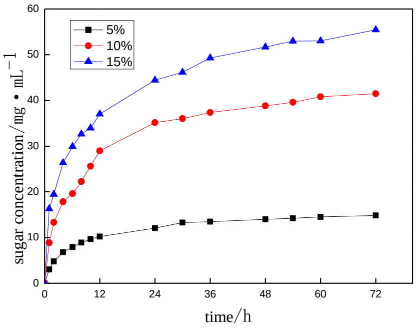

Figure 6: Sugar concentration change in enzyme hydrolysis process of different substrate concentrations

The time-dependent characteristic of apparent viscosity

After determining the slurry apparent viscosity, the author discovers that suspension viscosity reduces with the extension of measuring time. The time-dependent characteristic of apparent viscosity is identified under the following conditions: substrate concentration 5% (w/w) and temperature 20°C. The result is displayed in Figure 5. As a type of fiber suspension, the steam-exposed corn straw suspension features normal stress in addition to strong non-Newtonian fluid properties. In the NDJ–79 series rotary viscometer, the fibers in the suspension keep colliding and rolling during the rotation. Microscopically, the fiber orientations gradually shift to the same direction and draw closer to the velocity gradient plane. However, the apparent viscosity decreases macroscopically (Yang and Lin, 2011). Figure 5 also demonstrates that the suspension apparent viscosity eventually reaches a steady state. The time it takes to reach the stable value differs with the shear rate. The lower the shear rate, the shorter the time.

3.2 Different substrate concentrations in the enzyme hydrolysis process

3.2.1 Variation in sugar concentration with substrate concentration in enzyme hydrolysate:

Figure 6 displays the sugar concentration change curves in enzyme hydrolysates of 5%, 10% and 15% (w/w) substrate concentrations throughout the enzyme hydrolysis process.

In the three enzyme hydrolysates of different substrate concentrations, the sugar concentration follows the same change trend over the time (Figure 6): it increases quickly in the initial stage and grows at a slower pace after a period of time. For instance, the sugar concentration in the enzyme hydrolysate of 5% substrate concentration undergoes no significant changes after 48h. From 48h to 72h, the sugar concentration only grows by 5.86%. The growth range in the same period of time is 6.88% and 7.25% respectively for the enzyme hydrolysates of 10% and 15% substrate concentrations. This means the enzyme hydrolysis at 48h is more complete at a lower substrate concentration. The slowdown of sugar concentration increase is resulted from the lack of direct contact between cellulose enzyme and cellulose in the late phase of the reaction when the substrate concentration remains on a low level.

3.2.2 Variation in apparent viscosity with substrate concentration in enzyme hydrolysate:

Figure 7 shows the apparent viscosity change curves (shear rate 836 s^{-1}) in enzyme hydrolysates of 5%, 10% and 15% (w/w) substrate concentrations throughout the enzyme hydrolysis process.

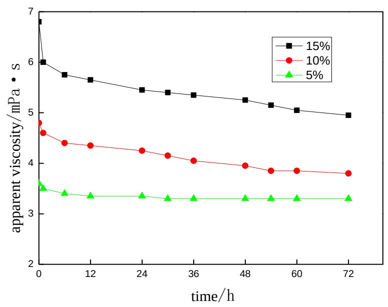

Figure 7: The change of apparent viscosity in enzyme hydrolysis process of different substrate concentrations

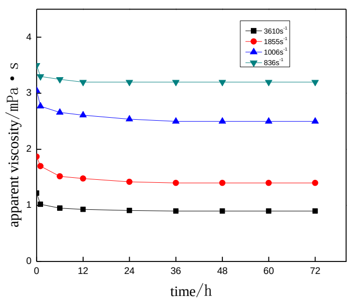

Figure 8: The change of apparent viscosity in enzyme hydrolysis process

As shown in Figure 7, the apparent viscosity of enzyme hydrolysate goes down with the development of enzyme hydrolysis. The sharpest decline occurs within 1h, and the decrease slows down after the 1 hour mark. After 36h, there is no significant changes to the apparent viscosity of the enzyme hydrolysate of 5% substrate concentration. As for the enzyme hydrolysate of 10% substrate concentration, the apparent viscosity no longer changes after 54h. When it comes to the enzyme hydrolysate of 15% substrate concentration, however, the apparent viscosity keeps falling throughout the reaction. The above phenomena are attributable to the gradual decline in substrate particle size in the reaction process. At a low substrate concentration, there is a small change for substrate particles to collide with each other. Thus, the continuous decrease of substrate particle size has little influence on the apparent viscosity in the late phase of enzyme hydrolysis process. There more chances for collision due to narrow of intermolecular distance when he substrate concentration is 15%. In this case, the apparent viscosity is reduced in the late phase of enzyme hydrolysis despite the falling particle size.

Figure 7 also reveals that the reduction in apparent viscosity varies with the substrate concentration. While the apparent viscosity in the enzyme hydrolysate of 5% substrate concentration declines by a small amplitude

(8.33%), that of 10% and 15% substrate concentrations decreases by 20.83% and 27.21% respectively. During the enzyme hydrolysis process, the decline in apparent viscosity is intensified with the increase in substrate concentration. This means the rheological properties of enzyme hydrolysate are increasingly under the influence of solid particles as the substrate concentration grows.

3.2.3 Rheological properties of enzyme hydrolysate

The apparent viscosity change trend in steam-exposed corn straw enzyme hydrolysate of 5% (w/w) substrate concentration is depicted in Figure 8. As shown in Figure 8, the apparent viscosity of enzyme hydrolysate decreases with the increase in shear rate during the reaction. The main reason is that cellulose is gradually catalyzed into soluble reducing sugar by cellulose enzyme, resulting in gradual decline in solid content. With the slow hydrolysis of cellulose, the solid particle size in the suspension gradually falls, reducing the chances of mutual winding and collision between fibrous particles. In addition, the figure shows that the apparent viscosity of enzyme hydrolysate changes at the fastest rate at 1h at whatever the shear rate. At that moment, the enzyme hydrolysis also reaches the peak speed. The above analysis indicates that the apparent viscosity of enzyme hydrolysate decreases with the increase of the shear rate (Figure 8). The relationship bears the features of pseudo-plastic fluid and can be fitted with Formula 4.

4. Conclusions

The apparent viscosity of steam-exposed corn straw suspension increases with the substrate concentration and shear rate. The apparent viscosity of the steam-exploded corn straw suspension also increases with the extension of shear time. This is because the fiber orientations are increasingly consistent in the suspension, leading to the inevitable reduction of macroscopic apparent viscosity. The enzyme hydrolysis witnesses the gradual increase of the sugar concentration in the enzyme hydrolysate of steam-exploded corn straw, and the slow decrease in the apparent viscosity. For the enzyme hydrolysate of substrate concentration 5% (w/w), the apparent viscosity barely changes after 36h of enzyme hydrolysis; the apparent viscosity shows a downward trend in enzyme hydrolysates of substrate concentration 10% and 15%. The variation in apparent viscosity is explained by the growing influence of solid particles on fluid apparent viscosity with the increase in the substrate concentration.

References

Ehrhardt M. R., Monz T. Q., Root T. W., 2010, Rheology of dilute acid hydrolyzed corn stover at high solids concentration, Applied biochemistry and biotechnology, 160 (4),1102-1115

Ghose T.K., 1987, Measurement of cellulase activities, Pure and Applied Chemistry, 59 (2), 257-268

Kyle M.D., Rajesh K.D., Nicholas G.B., 2010, Characteristics of changes in viscosity and insoluble solids content during enzymatic saccharification of pretreated corn stover slurries, Bioresource Technology, 101(10), 3575-3582

Liu L.P., Ma X.J., 2003, Study on Rheological Properties of Wheat Flour Saccharification Liquor , Bulletin of Science and Technology, 19(4), 306-308

Mat G, Guido Z. 2007, Pretreatment of lignocellulosic materials for efficient bioethanol production, Advances in Biochemical Engineering Biotechenology, 108, 41-65

Mustafa B., 2011, Production of bioethanol from lignocellulosic materials via the biochemical pathway. A review, Energy Conversion and Management, 52, 858-875

Natalia V.P., Thomas R.H., 2003, Measurement of rheological characteristics of corn stover suspensions, Applied biochemistry and biotechnology, 106, 383-392

Natalia V.P., Thomas R.H., 2004, Effect of corn stover concentration on rheological characteristics, Applied biochemistry and biotechnology, 114, 347-360

Ren Y., Wei A., Zhang D., 2007, Rheological characteristics of coal hydro-liquefaction residue, Journal of Fuel Chemistry and Technology, 35(3), 262-267

Saha K., Maheswari U. R., Sikder J., 2017, Membranes as a tool to support biorefineries: Applications in enzymatic hydrolysis, fermentation and dehydration for bioethanol production, Renewable & Sustainable Energy Reviews, 74, 873-890

Sridhar V., James D. M., Daniel J. S., 2009, Rheology of corn stover slurries at high solids concentrations-effect of saccharification and particle size, Bioresource Technology, 100(2),925-934

Yang R.D., Chen K.F., Li Z.Q., 2002, Rheological Properties and the Dependence of Viscosity on Temperature of Bagasse Black Liquor With High Consistency, Transactions of China Pulp and Paper, 17 (2), 53-55

Yang W., Lin J.Z., 2011, Research on the fiber orientation distributionand rhelogical property in the fiber suspensions, Chinese Journal of Hydrodynamics, 26(1), 116-122