Biochemical Engineering Journal 105 (2016) 412–419

Contents lists available at ScienceDirect

Biochemical Engineering Journal

journal homepage: www.elsevier.com/locate/bej

Regular article

Rheology evolution and CFD modeling of lignocellulose biomass during extremely high solids content pretreatment

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ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form 3 October 2015
Accepted 26 October 2015
Available online 30 October 2015

Keywords:
Lignocellulose
High solids content pretreatment
Evolution
Rheological properties
Computational fluid dynamics (CFD)
Reactor design

ABSTRACT

Design of industrial scale pretreatment reactors requires the accurate physical and rheological parameters of lignocellulose biomass. Rheological properties of raw and pretreated lignocellulose materials had been characterized in previous studies. A large gap of rheological properties between the raw and pretreated lignocellulose raised a difficulty for designing proper pretreatment reactors with maximum efficiency and minimum power consumption. In this study, the dilute acid pretreatment was operated in a 20-L reactor equipped with helical ribbon impeller agitation at high solids content up to 70% (w/w) dry solids. The operation was stopped at different time points, and then the completely or incompletely pretreated lignocellulose materials were released and sent for rheological property measurement. The changing rheological properties of lignocellulose materials were recorded into an evolution profile. The apparent viscosity change was found to be closely related to pretreatment temperature, and then affected the consequent enzymatic hydrolysis yield. The dynamic rheological parameters were fitted into power law model and the CFD model was established for high solids content pretreatment and used for industrial reactor design. Furthermore, the apparent viscosity of the raw and pretreated corn stover and wheat straw increased, instead of decreased, raising an instinct difference with the system of rigid solid particles and water. The study provided the first insight into the evolution of rheological properties during the high solids content pretreatment and the basis for industrial scale pretreatment reactor design.

1. Introduction

Pretreatment of lignocellulose breaks down the rigid lignin shell, deforms crystalline cellulose, and partial hydrolyzes hemicellulose. It is the central step of lignocellulose biorefinery process for biofuels and biochemical production. The latest advance of pretreatment technology tends to operate under high solids content for the purpose of reduction of waste water generation and steam consumption [1,2]. When solids content in pretreatment reactors is up to 50–70% (w/w), the limited amount of water and steam consumption is quickly and completely absorbed by solid lignocellulose materials and the whole materials system is composed of dry solid particles and fibers. This scenario is completely different with the liquid slurry system as in the case of low solids content pretreatment.

Design of industrial scale pretreatment reactors requires the accurate measurement of physical and rheological properties of lignocellulose materials used [3]. The rheological properties of raw lignocellulose material revealed that the long and soft fiber containing material system behaved interesting differences with common liquid–solids mixing system [4]. On the other hand, the rheological properties of pretreated lignocellulose material had been well characterized. Magnus et al. [5] studied the rheological properties of dilute acid pretreated spruce softwood at 6–12% insoluble solid content and found that the rheology property was strongly dependent on the water insoluble solids concentration. Lavenson et al. [6] measured the yield stress values of pretreated corn stover materials by magnetic resonance imaging at the solids content less than 10% (w/w). Sridhar et al. [7] measured the apparent viscosity and yield stress of dilute acid pretreated corn stover materials 10–40% (w/w) solids concentration, and found that these properties increased significantly with increasing solid concentration. Stickel et al. [8] studied the rheological properties of pretreated corn stover up to 30% insoluble solids, and found that the slurry was strongly shear-thinning, viscoelastic, and the yield stress was significantly concentration-dependent. Roche et al. [9] investigated the enzymatic hydrolysis of dilute acid pretreated corn stover at insoluble solids loadings of 20%, and developed the semi-empirical

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http://dx.doi.org/10.1016/j.bej.2015.10.021
1369-703X/

Nomenclatures

Latin symbols

d	the impeller diameter (m)
D	the reactor diameter (m)
C	geometric dimension parameter
H	the camber height of tank (m)
K_p	consistency coefficient ($\mathrm{Pa}\cdot\mathrm{s}^n$)
K_s	Metzner constant
l	the immersed height of helical ribbon (m)
M	torque ($\mathrm{N}\cdot\mathrm{m}$)
T_i	loading torque at i rpm ($\mathrm{N}\cdot\mathrm{m}$)
T_{io}	idle torque at i rpm ($\mathrm{N}\cdot\mathrm{m}$)
n	power-law index
N	the impeller rotation rate (rev/s)
N_p	dimensionless power number
N_r	the number of helical ribbon
P	power consumption (w)
R_{em}	Reynolds number (−)
s	pitch size of the helical ribbon (m)
S_e	diameter ratio for equivalent coaxial cylinders
w	ribbon width (m)
x	a dimensionless factor

Greek symbols

γ	apparent shear rate (s^{-1})
η_a	apparent viscosity ($\mathrm{Pa}\cdot\mathrm{s}$)
ρ	density of fluids ($\mathrm{kg/m}^3$)

relationship for correlating the enzymatic hydrolysis process with the particle concentration and yield stress. These works on rheological properties of pretreated lignocellulose materials were carried out at relatively low solids content system, which was still in a liquid slurry form. However, the rheological studies on extremely high solids content pretreatment, such as the one termed as "dry dilute acid pretreatment (DDAP)" without liquid phase existence [10,11], was still not yet investigated although the method produced significant high titer and yield of ethanol from corn stover feedstock [12].

Generally speaking, a large gap of rheological properties between the raw and pretreated lignocellulose exists, especially for advanced high solids content pretreatment systems. The gap indicates that the rheological property of lignocellulose experiences a significant change during pretreatment, but has not yet been characterized. The situation raises a difficulty for designing proper pretreatment reactors with maximum efficiency and minimum power consumption.

In this study, the dilute acid pretreatment was operated in a 20-L reactor equipped with helical ribbon impeller agitation and high pressure steam jetting apparatus at extremely high solids content up to 70% (w/w) dry solids. The operation was stopped at different time points, then the completely or incompletely pretreated corn stover materials were released and sent for rheological property measurement and its rheological property evolution of during pretreatment. The apparent viscosity change was found to be closely related to pretreatment temperature, and then affected the consequent enzymatic hydrolysis yield. The results indicated a certain high temperature was required for maintaining pretreatment efficiency from the aspect of rheology change. The dynamic rheological parameters were fitted into power law model and the CFD model was established for high solids content pretreatment and used for industrial reactor design. Furthermore, the apparent viscosity of the raw and pretreated corn stover and wheat straw increased, instead of decreased, raising an instinct difference with the system of rigid solid particles and water. The study provided the first insight into the evolution of rheological during the high solids content pretreatment and the basis for industrial scale pretreatment reactor design.

2. Materials and methods

2.1. Raw materials and physical property measurement

Corn stover and wheat straw were harvested in Dancheng, Henan, China in 2012. The compositions of the raw materials were measured using according to NREL LAP protocols [13,14]. Wheat straw contained 41.30% of cellulose, 31.90% of hemicellulose. Corn stover contained 36.18% of cellulose and 19.83% of hemicellulose.

The materials were washed to remove the field dirt, stones and metals and dried, then milled using a beater pulverizer and screened through a mesh with the circle diameter of 10 mm. The milled raw materials were stored in sealed plastic bags for use.

2.2. Physical property measurements

The size distribution of milled materials was measured using norm sample sieves. Eight size of norm sample sieves were selected, 10 meshes, 10–20 meshes, 20–40 meshes, 40–60 meshes, 60–80 meshes, 80–100 meshes, and larger than 100 mesh per square inch, corresponding to fractions of 2.00 mm, 1.42 mm, 0.63 mm, 0.34 mm, 0.21 mm, 0.17 mm and 0.15 mm in mean diameter of the particles to be measured.

The raw and pretreated materials bulk density was measured in a 1000 mL flask with 120 mm diameter and adequately mixed to obtain 0%, 10%, 30%, 50% and 70% water content materials. Each sample was mass measured and the occupied volume was calculated repeatedly three times to calculate bulk density using the mass to volume ratio.

2.3. Enzyme and reagents

The cellulase enzyme Youtell #6 was provided by Hunan Youtell Biochemical Co., Yueyang, Hunan, China. The filter paper activity was 135 FPU/g determined according to NREL LAP-006 [15], and the cellulase activity was 344 cellobiase units (CBU/g) using the method described by Ghose [16]. The protein concentration of the cellulose used was 90 mg/g cellulase determined by Bradford assay using bovine serum albumin (BSA) as protein standard.

All chemicals including H_2SO_4, NaOH, $CaCO_3$ and citric acid were purchased from the local supplier Linfeng Chemical Reagent Co., Shanghai, China. Tetracycline was purchased from Sigma–Aldrich Co., St. Louis, MO, USA.

2.4. Pretreatment operation

Corn stover and wheat straw were pretreated using dry dilute sulfuric acid pretreatment (DDAP) according to Zhang et al. [17] and He et al. [11]. Briefly, 1400 g of dried corn stover (or 1200 g of dried wheat straw) and 700 g for corn stover (or 600 g for wheat straw) of 5% (w/w) dilute sulfuric acid solution were co-currently fed into the reactor in 20 L vol to reach the solid/liquid ratio of 2:1 (w/w) under helically agitated mixing at 50 rpm for 3 min. The pretreatment operation started by jetting the 1.6 MPa hot steam on the well mixing corn stover or wheat straw materials inside the reactor. The experiment of dry dilute sulfuric acid pretreatment of corn stover or wheat straw feedstock started from the point of steam jetting onto corn stover in the reactor and was set to 11 min in this study. In the first 3 min, the feedstock was heated to approximately 150 °C; in the second 3 min, the temperature was elevated from 150 °C to 175 °C (the required pretreatment temperature); in the last 5 min, 175 °C was maintained till the end of one batch operation of pretreatment. For investigating the evolution of physical and rheological properties during the pretreatment, the operation was stopped by suspending the steam jetting and releasing reactor pressure at each of the three time points: 3, 5, and 11 min after the steam was jetted on the feedstock materials. The pretreated materials were removed from the reactor by gravity to a collection box.

Totally the pretreated feedstock streams contained 50% of solids and 50% of liquid by weight percentage. Due to the high absorption capacity of lignocellulose materials, the liquid was absorbed into the solid to generate the pretreated feedstock at approximately 50% (w/w) of solids and no free liquid stream was generated. The solid portion of the pretreated corn stover contained 38.18% of cellulose, 2.13% of hemicellulose. The solid portion of the pretreated wheat straw contained 45.39% of cellulose, 3.83% of hemicellulose.

The pretreatment efficiency of pretreated corn stover and wheat straw was assayed by enzymatic hydrolysis using NREL LAP-009 [18]. Briefly, 1.0 g of pretreated corn stover or wheat straw was hydrolyzed at 2.5% (w/w) solids content, 20 FPU/g DM at 50 °C and pH 4.8 for 72 h. The cellulose conversion of corn stover and wheat straw were 97.88% and 96.14%, respectively.

2.5. Determination of rheological properties

Raw and pretreated materials at high solids content were in the format of solid particles thus the apparent viscosity could not be measured by ordinary rheometer. The study using a specially designed 5 L helical ribbon stirred reactor equipped with a torque meter was used for determination of apparent viscosity of raw and pretreated materials (corn stover or wheat straw) as described in Zhang et al. [4]. The reactor work volume, reactor diameter, impeller diameter and impeller total high were 3 L, 168 mm, 151 mm and 114 mm, respectively. The motor was mounted on the top of the impeller to form axial upwelling flow. The torque meter HX-901 (Huaxin Mechanical and Electrics Co., Beijing, China) was installed onto the reactor for measurement of agitation torque. The phenomenon of shear-induced materials migration generally existed at agitation mixing system was not considered during apparent viscosity measurement. The temperature change from mechanical friction during the mixing was ignored. The torque was recorded every 5 s for 8–10 min at each agitation rate in the range of 50–130 rpm. The zero torque value with empty material feeding was recorded as T_{io}. The torque after the materials were added into the reactor was recorded as T_i. The true torque value on mixing was defined as $M = T_i - T_{i0}$.

Lignocellulose materials were compressible due to the bulk density increase during pretreatment processes, but they were assumed as incompressible and continue fluid at special pretreatment time. The dimensionless power number N_P was expressed as the function Reynolds number Re_m under the laminar flow [19]:

$$N_p = C \times Re_m^x \tag{1}$$

where C is a geometry parameter of the reactor used and independent of the fluid properties, x is a dimensionless factor. $C = 147.12$ and $x = -1$ were measured at this bioreactor [4]. The Re_m value for a non-Newtonian fluid system under laminar flow condition and the N_p value under different rotation rates were calculated by Eqs. (2)–(3) according to Chen [20] and Paul et al. [21]. The maximum Reynolds number in these materials mixing system was 16.93, indicating that laminar flow assumption was suitable.

$$N_p = \frac{P}{\rho N^3 d^5} = \frac{2\pi NM}{\rho N^3 d^5} = \frac{2\pi M}{\rho N^2 d^5} \tag{2}$$

$$Re_m = \frac{\rho N d^2}{\eta_a} \tag{3}$$

where P is the power consumption of stirred impeller (W), ρ is the density of the fluid (kg/m^3), N is the impeller rotation rate (rev/s), d is the impeller diameter (m), η_a is the apparent viscosity (Pa · s).

Combining Eqs. (1)–(3) gave the calculation of the apparent viscosity η_a [4]:

$$\eta_a = \frac{2\pi M}{CNd^3} = \frac{\pi M}{73.56Nd^3} \tag{4}$$

The pseudo properties of pretreated materials could be well described by the power law model, where Kp was the consistency coefficient (Pa · s^n), n was the dimensionless power-law index, γ was the apparent shear rate (s^{-1}) [22–24]. The linearized power law model was shown in Eq. (5):

$$\begin{aligned}\log_{10}\eta_a &= \log_{10}K_P + (n-1)\times\log_{10}(K_S \times N) = \\ &[\log_{10}K_P + (n-1)\times\log_{10}K_S] + (n-1)\times\log_{10}N\end{aligned} \tag{5}$$

where the apparent shear rate $\gamma = K_s \times N$ [25], N was the impeller rotation rate (rev/s), K_s was the Metzner constant and expressed according to Delaplace et al. [26] in Eqs. (6) and (7) .

$$K_s = \frac{2}{N_r}\,\frac{S^{2/n}}{S^2}\,\frac{S_e^2 - 1}{S_e^{2/n} - 1}\,\frac{C}{\pi^2\left(l/d\right)}\left[\frac{n}{2-n}\,\frac{S^{(2/n)-1}}{S-1}\right]^{1/(n-1)} \tag{6}$$

$$S_e = \frac{D}{d_e} = \frac{S}{2w/d} \Big/ \ln\left(\frac{S - \left(1 - 2w/d\right)}{S-1}\right) \tag{7}$$

where S is the diameter ratio of D/d of the helical ribbon impeller, w is ribbon width (m), d is the impeller diameter (m), l is the immersed height of helical ribbon (m), D is the reactor diameter (m), Nr is the number of helical ribbon.

For a specific stirred vessel and fluid, the power-law index n and K_s value was constant. The n value was calculated by the slope value of linearized power law Eq. (5) using the logarithm of agitation rates (50–130 rpm) as independent variable and the logarithm of apparent viscosity as dependent variable. The K_s value was calculated by Eqs. (6)–(7) using the n value and the consistency coefficient K_p was calculated by the intercept of Eq. (5).

2.6. CFD modeling

A commercial grid-generation tool ICEM CFD 14.0 (Ansys Inc.) was used to generate the 3D grids of the reactor model in Autodesk Inventor 2014 (Autodesk Inc.) for running Fluent software (version 14.0). The mathematical model was characterized with the Multiple Reference Frame model (MRF), where impeller rotation was set as the move zone and other regions were set as the tank zone. The upper surface of the liquid was defined as free, and a non-slip wall condition was used for both the walls and the surface of the impellers. The model solved as implicit and pressure-based was based on the following assumptions:

(1) Define the materials as incompressible and non-Newtonian single phase fluid under laminar flow conditions, neglecting chemical reaction and steam effect.
(2) Neglecting temperature effect for mixing time and power consumption.
(3) Iteration error for calculating mixing time is set as 1×10^{-4}.
(4) The tracer has the same physical properties as the background fluid, and the mass fraction of the tracer in the injected area equals to 1 at the beginning of the agitation while at all other areas equal to 0.

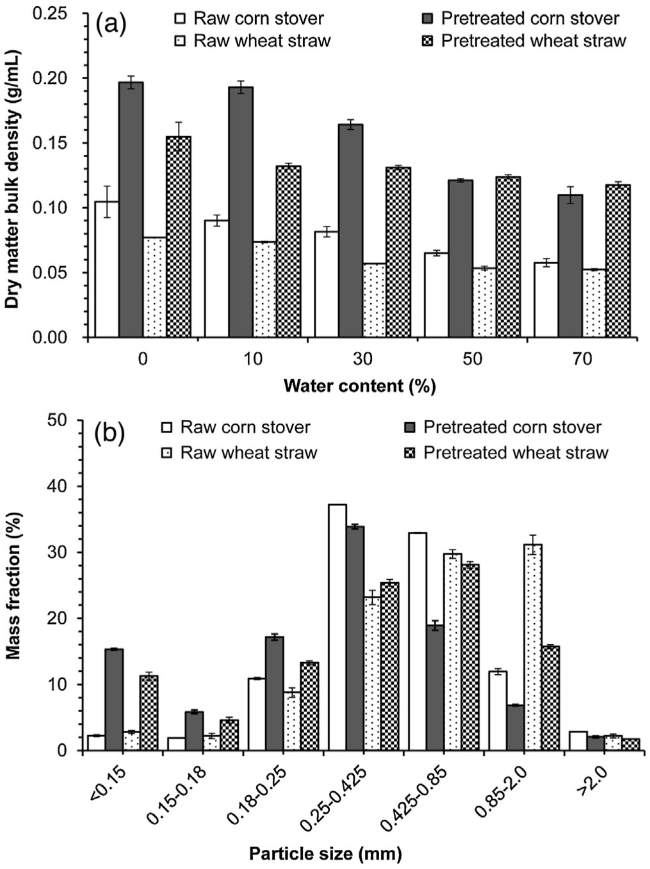

Fig. 1. Dry matter bulk density (a) and particle size distribution (b) of corn stover and wheat straw. Both corn stover and wheat straw were pretreated at 175 °C for 5 min at the initial solid/liquid ratio of 2:1.

For evaluation the mixing efficiency at different geometrical structures, degree of homogeneity ($M(t)$) was defined as:

$$M(t) = \frac{|c_i(t) - c_{ave}|}{c_{ave}} \times 100\% \qquad (8)$$

where $c_i(t)$ is the tracer concentration, and c_{ave} is the average tracer concentration throughout the entire computational domain. The mixing time was defined as the time required to achieve $M(t) \leq 5\%$.

Pretreatment reactor was internal pressure-bearing equipment with elliptical head used S30408 austenitic stainless steels according to Pressure Vessel Handbook. The high of elliptical head (h), screw pitch (s), impeller diameter (d) and ribbon width (w) of the reactor directly impacting mixing effect and power consumption were optimized by CFD simulation.

3. Results and discussion

3.1. Physical and rheological property characterization of raw and pretreated lignocellulose

Bulk density of lignocellulose biomass determines the volumetric loading capacity of pretreatment reactors. Fig. 1a shows the bulk density of corn stover and wheat straw at water content from 0% to 70% (at dry basis) before and after dry dilute acid pretreatment. The water content range was given based on the practical pretreatment operation under high solids content [2]. Further increase of water content over 70% led to the appearance of free water accumulating on the reactor bottom. This was conflict with the free water generation in the dry dilute acid pretreatment as an environmentally friendly process. The bulk density of pretreated corn stover (dry base) increased approximately one fold than that of raw corn stover at varied water contents. Wheat straw showed the similar tendency of bulk density increase. The results indicate that lignocellulose feedstock could be pretreated near the collection locations then transported to the biorefinery plant for processing. In this way, the logistic cost is reduced by transporting pretreated feedstock with high density, instead of raw feedstock with low density. The bulk density increase of pretreated materials was confirmed by comparing the particle size distribution of raw materials with that of pretreated materials (Fig. 1b). In addition, corn stover and wheat straw, either the raw or the pretreated, showed the declining dry matter bulk density with increasing water content, perhaps due to the fiber expansion at higher water content.

The apparent viscosity of the raw and pretreated materials at varied water contents were calculated based on measured torque values (Fig. 2). The apparent viscosity of corn stover (Fig. 2a for the raw and Fig. 2c for the pretreated) and wheat straw (Fig. 2b for the raw and Fig. 2d for the pretreated) steadily increased with increasing water content at each agitation rate. This is surprisingly different from the viscosity tendency of rigid solid particles mixing with water, in which the increased water leads to the decrease of apparent viscosity due to the lubricant function of water added [4]. The phenomenon may be explained by unique property of lignocellulose materials: fiber particles of corn stover, wheat straw, or other lignocellulose biomass are not rigid solids and are able to absorb water quickly up to 10 folds of its dry weight. Thus the free water doesn't exist at these mixing systems and is not able to act as lubricant. Instead, intertwined and entangled long fibers form complicated mesh structures and block the movement of fiber particles. Fibers also swell with increased water content and increase the friction of fiber particles. For pretreated corn stover or wheat straw, formation of oligo sugars and monosaccharide from hemicellulose hydrolysis could act as adhesives, instead of lubricants. Furthermore, the fiber particles in the sticky slurry increase the strength in a similar way to concrete structure. As the result, the apparent viscosity increases with increasing water content until sufficient water addition leads to the appearance of free water, which it is not in the range of the present high solids content pretreatment concerned.

The apparent viscosity of pretreated corn stover (Fig. 2c) was approximately three folds greater than that of raw corn stover (Fig. 2a) at the fixed water content and agitation rate due to the more compact bulking and smaller particle size. Similar to raw corn stover, the apparent viscosity of pretreated wheat straw increased with increasing water content at varied agitation rate, and decreased with increasing agitation rate at varied water content (Fig. 2b and d). The apparent viscosity of pretreated wheat straw at varied water content and agitation rate (Fig. 2d) was close to that of corn stover (Fig. 2c). The apparent viscosity of corn stover (both the raw and the pretreated) was slightly greater than that of wheat straw.

The apparent viscosity of corn stover (Fig. 2a and c) and wheat straw (Fig. 2b and d) decreased with increasing agitation rate at each water content, indicating that the pseudo fluids of corn stover and wheat straw materials (both the raw and the pretreated) behaved shear thinning non-Newtonian properties.

The n and K_P values of corn stover and wheat straw (the raw and the pretreated) were calculated as shown in Fig. 3. The n values at each case were in the range of 0.05–0.30, indicating the typical shear thinning property of these pseudo fluids. The K_p values increased with increasing water content, identifying the viscosity increase with water content increasing. A direct experimental observation on the material adherence to the reactor wall was worsened under greater water content, giving the further evidence for increased viscosity with greater water content. The n values of

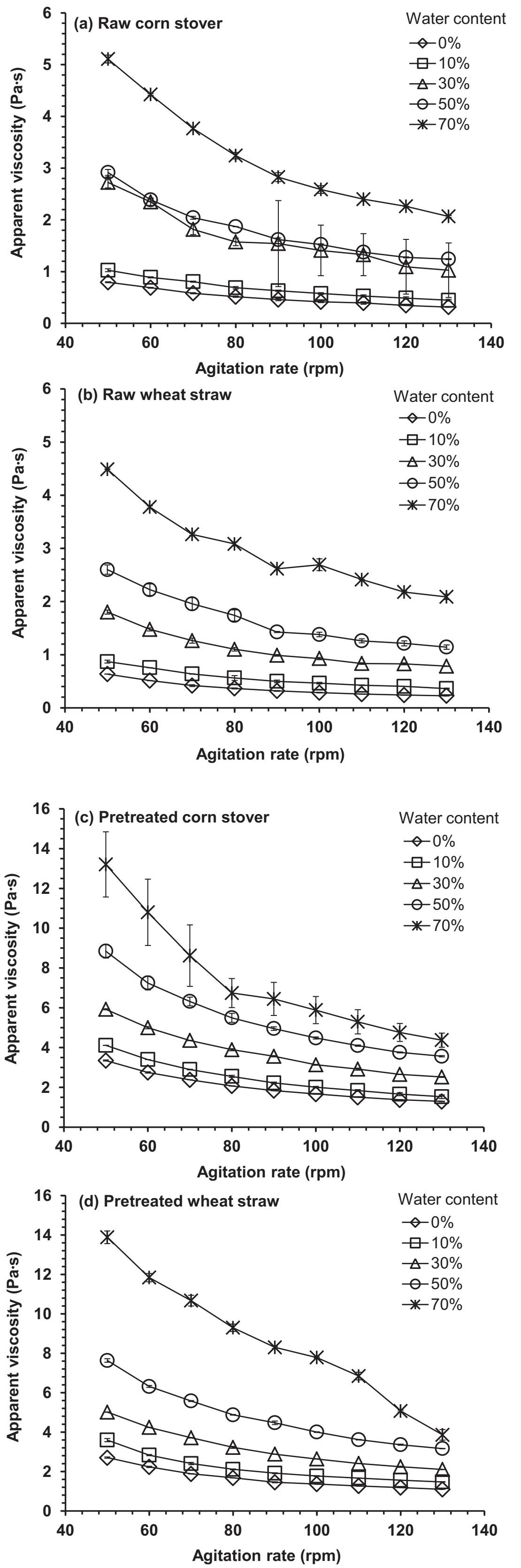

Fig. 2. Apparent viscosity of raw corn stover (a), raw wheat straw (b), pretreated corn stover (c), and pretreated wheat straw (d) with varied water contents and agitation rates. The experiments were carried out at ambient temperature (25 °C) in a 5 L helical impeller agitating reactor equipped with a torque meter.

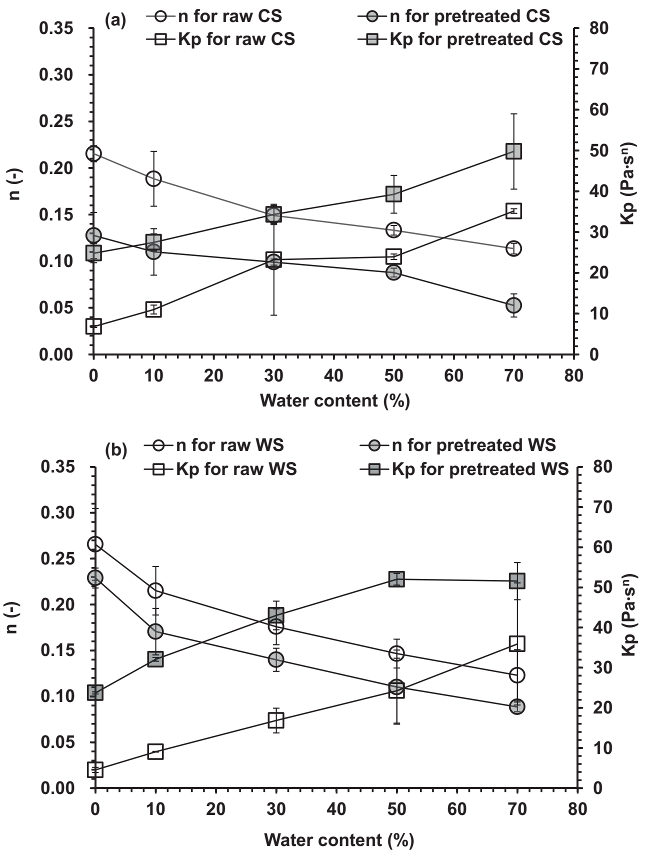

Fig. 3. Determination of rheological parameters of raw and pretreated corn stover (a), as well as raw and pretreated wheat straw (b) at different water contents. Measurement at ambient temperature (25 °C) in a 5 L helical impeller reactor equipped with a torque meter.

the pretreated corn stover or wheat straw were smaller and the K_p value were greater than that of the virgin corn stover, which was in agreement of the above analysis on apparent viscosity.

The results reveal that pretreatment at high solids content of corn stover or wheat straw not only changed their chemical and physical properties (such as bulk density and particle size), but also changed the rheological properties significantly (such as viscosity, n and K_p values). The rheological properties of these materials could be perfectly described by power law model of non-Newtonian fluid.

3.2. Evolution of rheological properties of lignocellulose during pretreatment and its CFD modeling

Evolution profiles of the rheological properties of corn stover during high solids content pretreatment were recorded for the purpose of optimal design of mixing apparatus and geometric structure of pretreatment reactors. The operation of dry dilute sulfuric acid pretreatment of corn stover was stopped by suspending the steam jetting and releasing reactor pressure at each of the three time points: 3 min (pre-heating to 150 °C), 6 min (heating to 175 °C), and 11 min (maintaining for 5 min at 175 °C). Then the corn stover material was released from the reactor vessel and sent for rheological property measurement and pretreatment efficiency.

The water content of corn stover material increased from 33% (w/w) at the starting time until approximately 54% (w/w) at the end of pretreatment operation, due to the absorption of jetted steam (Fig. 4). The bulk density, both the apparent wet bulk density and the dry matter bulk density, increased with the pretreatment proceeded. The apparent viscosity of corn stover slowly increased from the starting temperature to 175 °C, and then quickly increased

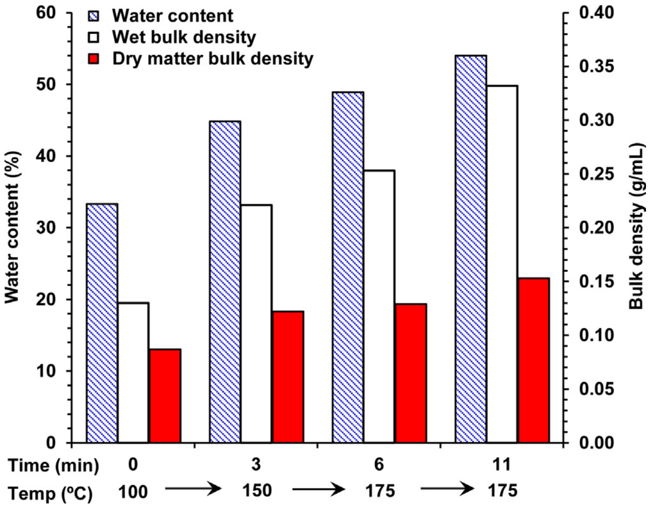

Fig. 4. Physical properties evolution of corn stover during the dry dilute acid pretreatment. The operation was carried out in a 20 L helically stirred reactor at 50 rpm and stopped at different times. The first 6 min was the heating time to the required temperature (175 °C), and latter 5 min was the pretreatment period at the given temperature. The corn stover samples were withdrawn at the time points of 3 min (heated to 150 °C), 6 min (175 °C), and 11 min (175 °C).

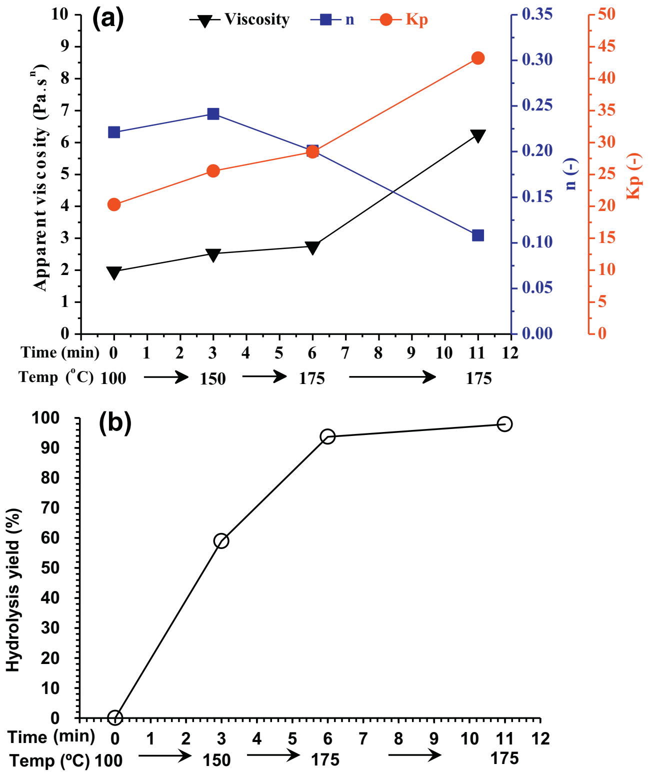

Fig. 5. Rheological properties evolution (a) and hydrolysis yield (b) of corn stover during the dry dilute acid pretreatment. The operation was carried out in a 20 L helically stirred reactor at 50 rpm and stopped at different times. The first 6 min was the heating time to the required temperature (175 °C), and latter 5 min was the pretreatment period at the given temperature. The corn stover samples were withdrawn at the time points of 3 min (heated to 150 °C), 6 min (175 °C), and 11 min (175 °C).

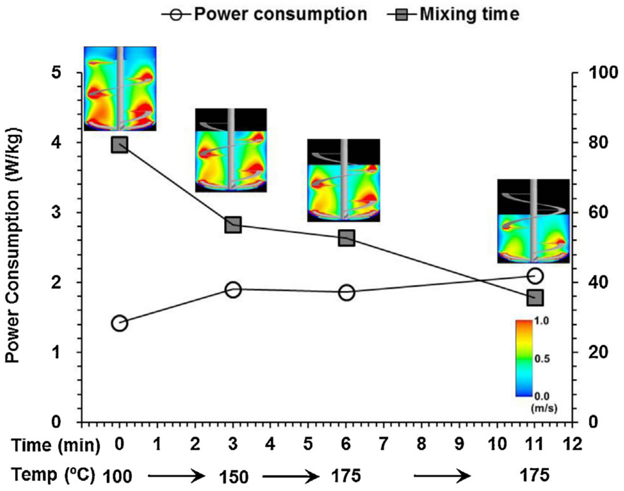

Fig. 6. Evolution of power consumption and mixing time of corn stover during dry dilute acid pretreatment in the 2.5 m^3 helically stirred reactor. The pretreatment was carried out at 175 °C for 5 min at 50 rpm agitation rate. The initial dry feedstock solid weight percentage was 33%. The sulfuric acid usage was 2.5% (w/w) of dry feedstock weight.

when the temperature was maintained at 175 °C for 5 min (Fig. 5a). The K_p value was in a similar tendency with apparent viscosity. On the other hand, the *n* value was approximately constant in the first 3 min, then decreased quickly in the period of temperature maintaining at 175 °C, indicating that enhanced shear thinning behaviors of corn stover used. The results suggest that the rheological properties of corn stover were highly dependent on pretreatment temperature. At the temperature below 150 °C, the rheological property was approximately constant, but quickly changed when it was increased to and maintained at 175 °C. The hydrolysis yield of pretreated corn stover was also in a similar evolution tendency (Fig. 5b), indicating that that efficient pretreatment should be operated under a certain high temperature from the aspect of rheology change.

Principally, both pretreatment temperature and time affect the rheology of lignocellulose feedstock, but the present results indicate that temperature played a more important role on rheology property change. Fig. 5 shows that during the first 3 min of pretreatment with the temperature change from 100 °C to 150 °C, and during the second 3 min with the temperature change from 150 °C to 175 °C, the apparent viscosity led to a limited change. During the third 5 min with temperature at 175 °C, the apparent viscosity changed greatly. The results may suggest that significant rheology change corresponds to a minimum temperature. Interesting, the hydrolysis yield did not accurately correspond to the rheology change: during the first 6 min, the apparent viscosity changed little but the hydrolysis yield increased significantly, while during the last 5 min, the apparent viscosity changed greatly but the hydrolysis yield changed little. Rheology change of a certain material generally indicates its structure change. In the hydrolysis of pretreated lignocellulose biomass, the significant hydrolysis yield change takes place ahead of rheology change, indicating the enzymatic hydrolysis is not as assumed in regular viewpoint that the structure change by pretreatment lead to the increased hydrolysis yield.

The evolution process of corn stover pretreatment was simulated by establishing CFD model based on the rheological model above. The reactor structure was assumed to the level of industrial scale with the volume of 2.5 cubic meters. The power consumption, mixing time and velocity field distribution at each pretreatment point were calculated (Fig. 6). With increased bulk density, the accumulative volume of corn stover decreased quickly in the pretreatment till approximately half of the starting volume of corn stover. The power consumption per kg of dry corn stover (w/kg) increased and the mixing time of corn stover decreased with the pretreatment operation proceeded. At the initial stage of pretreatment, the bulk density and viscosity were relatively low, resulting in power consumption lower although the velocity in the flow field

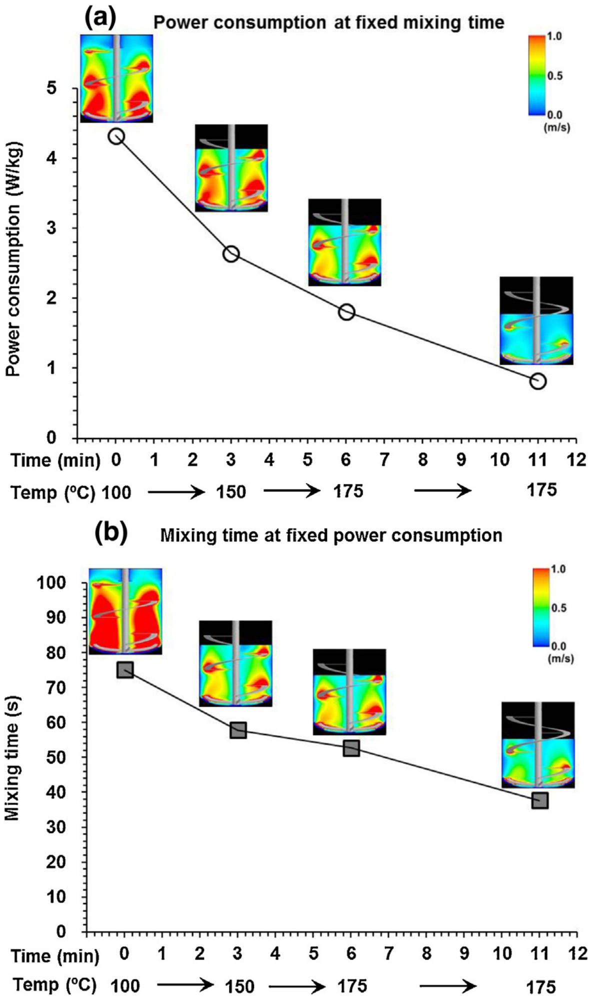

Fig. 7. CFD calculation of the power consumption at the fixed mixing time (50 s) and the mixing time at the fixed power consumption (1.8 W/kg) of corn stover during dry dilute acid pretreatment in the 2.5 m^3 helically stirred reactor. The pretreatment was carried out at 175 °C for 5 min at 50 rpm agitation rate. The initial dry feedstock solid weight percentage was 33%. The sulfuric acid usage was 2.5% (w/w) of dry feedstock weight.

was high. At the end of pretreatment, the increase of viscosity and the decrease of corn stover volume caused the increased power consumption and decreased mixing time. The results also reveals that when temperature was under a certain level (175 °C for corn stover used in this study, but may differ for varied biomass types), the pretreatment efficiency was low and the steam used was only for compensating the heat loss and increasing water content in the early stage of pretreatment. The accelerated heating rate to the required pretreatment temperature may help the elevation of pretreatment efficiency and reduce the steam energy usage.

Power consumption at a fixed mixing time (50 s) and mixing time at a fixed power consumption of 1.8 W/kg were calculated to show the changing tendency of mixing efficiency of corn stover in pretreatment reactor (Fig. 7). Power consumption decreased quickly at the fixed mixing time with changing physical and rheological properties in pretreatment (Fig. 7a). Mixing time also decreased at the fixed power consumption in pretreatment (Fig. 7b), but the change was not significant. This result may suggest that when helically agitation in the pretreatment reactor provided well mixing, power consumption should be the major consideration for high solids content pretreatment.

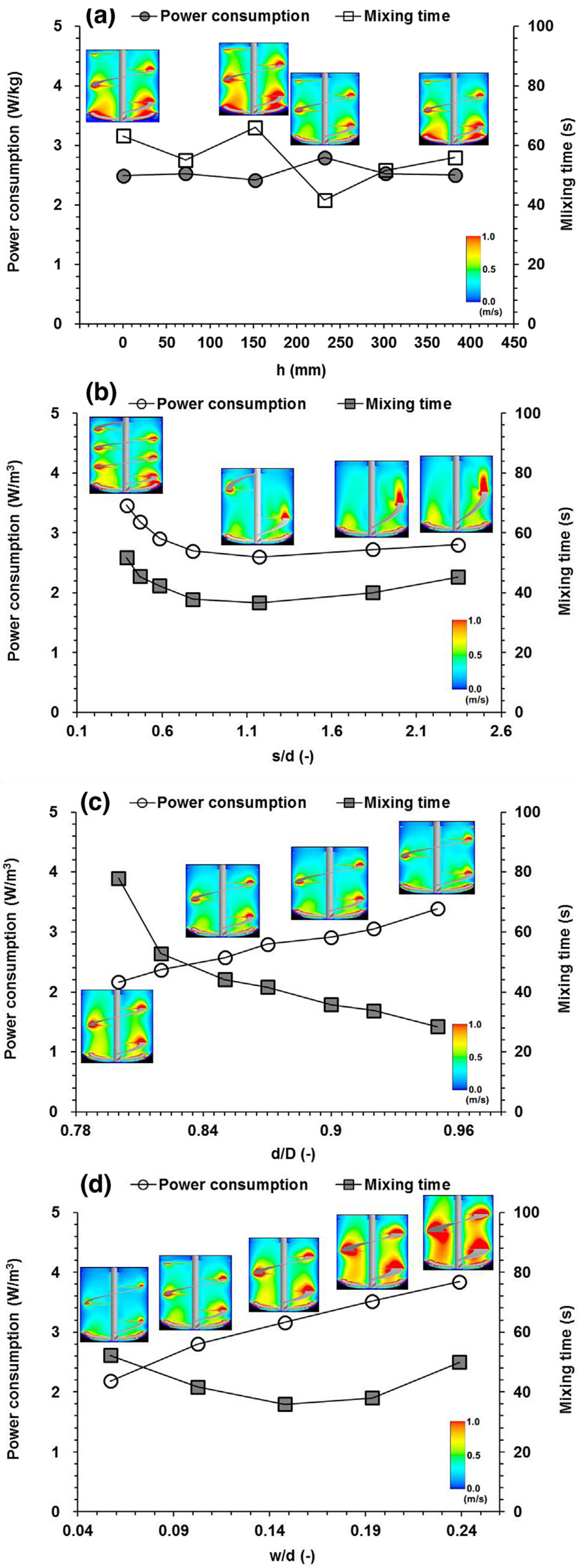

Fig. 8. Power consumption and mixing time with the changing structure parameters. (a) with changing camber height h, (b) with changing pitch of the helical ribbon impeller s, (c) with changing impeller diameter d, and (d) with changing ribbon width w. The reactor geometry is shown in Fig. 6. The pretreatment was carried out at 175 °C for 5 min at 50 rpm agitation rate. The initial dry feedstock solid weight percentage was 33%. The sulfuric acid usage was 2.5% (w/w) of dry feedstock weight.

3.2. Geometrical design and optimization of the industrial scale pretreatment reactors

The rheology model of corn stover with pretreatment evolution was applied to the design of an industrial scale pretreatment reactor with a volume of 2.5 cubic meters by CFD calculation. The geometrical structure parameters of the reactor were optimized for obtaining minimum power consumption and maximum mixing efficiency.

Power consumption and mixing time of pretreatment were not significantly changed with changing elliptical head height (h) of the helical ribbon impeller (Fig. 8a). Considering the practical manufacture limitation for pressure vessels, a proper h value of 232 mm was selected for the reactor used. Both the power consumption and mixing time decreased significantly with the increasing ratio of screw pitch height (s) to impeller diameter (d) in the range of 0.4–0.8, then kept approximately constant or slightly increased in the range of 1.2–2.4, indicating an optimal s/d range of 0.8–1.2 existed for the reactor (Fig. 8b). Power consumption steadily increased but mixing time sharply decreased with increasing ratio of impeller diameter (d) to reactor diameter (D) in the range of 0.8–0.95 (Fig. 8c). The impeller diameter increase caused a high shear rate and easily led to adherence of material to the wall. A proper d/D range was selected from 0.9 to 0.92 as optimal range for the reactor designed. Power consumption increased with increasing ratio of ribbon width (w) to impeller diameter (d), but mixing time increased with increasing w/d and then decreased (Fig. 8d). A proper w/d range from 0.1 to 0.15 was selected as optimal value.

Considering of power consumption, mixing effect and material adherence, as well as technical feasibilities, the structure parameters of 2.5 cubic meter reactor and helical ribbon impeller were designed based on the optimal calculation of CFD modeling. The method provided a basis of industrial pretreatment reactor design.

4. Conclusion

The physical and rheological properties of two typical lignocellulose materials, corn stover and wheat straw were measured before and after the extremely high solids content up to 70% (w/w) of dry solids. The apparent viscosity of the lignocellulose materials before and after pretreatment increased with increasing water content, raising an instinct difference with the system of rigid solid particles with water. The evolution of rheological properties of corn stover during high solid content pretreatment was recorded for the first time. Temperature was found to be the key parameter to affect the rheological properties and enzymatic hydrolysis yield. The dynamic rheological parameters were fitted into power law model and the CFD model was established for high solid content pretreatment and used for industrial reactor design.

Acknowledgements

This research was supported by the National Basic Research Program of China (2011CB707406), the Natural Science Foundation of China (21306048), the National High-Tech Program of China (2012AA022301/2014AA021901).

References

[1] A.A. Modenbach, S.E. Nokes, The use of high-solids loadings in biomass pretreatment—a review, Biotechnol. Bioeng. 109 (2012) 1430–1442.

[2] J. Zhang, W.L. Hou, J. Bao, Reactors for high solid loading pretreatment of pretreatment of lignocellulosic biomass, Adv. Biochem. Eng. Biotechnol. (2015), http://dx.doi.org/10.1007/10_2015_307.

[3] S. Senturk-Ozer, H. Gevgilili, D.M. Kalyon, Biomass pretreatment strategies via control of rheological behavior of biomass suspensions and reactive twin screw extrusion processing, Bioresour. Technol. 102 (2011) 9068–9075.

[4] L.P. Zhang, J. Zhang, C.H. Li, J. Bao, Rheological characterization and CFD modeling of corn stover-water mixing system at high solids loading for dilute acid pretreatment, Biochem. Eng. J. 90 (2014) 324–332.

[5] W. Magnus, P. Benny, T. Eva, L. Gunnar, Rheological characterization of dilute acid pretreated softwood, Biotechnol. Bioeng. 108 (2011) 1031–1041.

[6] M.D. Lavenson, E.J. Tozzi, M.J. McCarthy, R.L. Powell, Yield stress of pretreated corn stover suspensions using magnetic resonance imaging, Biotechnol. Bioeng. 108 (2011) 2312–2319.

[7] V. Sridhar, D.J. McMillan, D.J. Schell, R.T. Elander, Rheology of corn stover slurries at high solids concentrations—effects of saccharification and particle size, Bioresour. Technol. 100 (2009) 925–934.

[8] J.J. Stickel, J.S. Knutsen, M.W. Liberatore, W. Luu, D.W. Bousfield, D.J. Klingenberg, C.T. Scott, T.W. Root, M.R. Ehrhardt, T.O. Monz, Rheology measurements of a biomass slurry: an inter-laboratory study, Rheol. Acta 48 (2009) 1005–1015.

[9] C.M. Roche, C.J. Dibble, J.S. Knutsen, J.J. Stickel, M.W. Liberatore, Particle concentration and yield stress of biomass slurries during enzymatic hydrolysis at high-solids loadings, Biotechnol. Bioeng. 104 (2009) 290–300.

[10] Y.Q. He, J. Zhang, J. Bao, Dry dilute acid pretreatment by co-currently feeding of corn stover feedstock and dilute acid solution without impregnation, Bioresour. Technol. 158 (2014) 360–364.

[11] Y.Q. He, L.P. Zhang, J. Zhang, J. Bao, Helically agitated mixing in dry dilute acid pretreatment enhances the bioconversion of corn stover into ethanol, Biotechnol. Biofuels 7 (2014) 1.

[12] A.S. Qureshi, J. Zhang, J. Bao, High ethanol fermentation performance of the dry dilute acid pretreated corn stover by an evolutionarily adapted *Saccharomyces cerevisiae* strain, Bioresour. Technol. 189 (2015) 399–404.

[13] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of structural carbohydrates and lignin in biomass, in: Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory, Golden, CO, 2008.

[14] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, Determination of sugars, byproducts, and degradation products in liquid fraction process samples, in: Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory, Golden, CO, 2008.

[15] B. Adney, J. Baker, Measurement of cellulase activities, in: Laboratory Analytical Procedure (LAP-006), National Renewable Energy Laboratory, Golden, CO, 1996.

[16] T.K. Ghose, Measurement of cellulase activities, Pure Appl. Chem. 59 (1987) 257–268.

[17] J. Zhang, X. Wang, D. Chu, Y. He, J. Bao, Dry pretreatment of lignocellulose with extremely low steam and water usage for bioethanol production, Bioresour. Technol. 102 (2011) 4480–4488.

[18] L. Brown, R. Torget, Enzymatic saccharification of lignocellulosic biomass, in: Laboratory Analytical Procedure (LAP-009), National Renewable Energy Laboratory, Golden, CO, 1996.

[19] P.J. Carreau, R.P. Chhabra, J. Cheng, Effect of rheological properties on power consumption with helical ribbon agitators, AIChE. J. 39 (1993) 1421–1430.

[20] Y.R. Chen, Impeller power consumption in mixing livestock manure slurries, Trans. ASAE 24 (1981) 187–192.

[21] E.L. Paul, V.A. Atiemo-Obeng, S.M. Kresta, Handbook of Industrial Mixing, Wiley, New York, 2004.

[22] R.K. Dasari, K. Dunaway, R.E. Berson, A scraped surface bioreactor for enzymatic saccharification of pretreated corn stover slurries, Energy Fuels 23 (2009) 492–497.

[23] J. Du, F.Z. Zhang, Y.Y. Li, H.M. Zhang, J.R. Liang, H.B. Zheng, H. Huang, Enzymatic liquefaction and saccharification of pretreated corn stover at high-solids concentrations in a horizontal rotating bioreactor, Bioprocess. Biosyst. Eng. 37 (2014) 173–181.

[24] K.W. Dunaway, R.K. Dasari, N.G. Bennett, R.E. Berson, Characterization of changes in viscosity and insoluble solids content during enzymatic saccharification of pretreated corn stover slurries, Bioresour. Technol. 101 (2010) 3575–3582.

[25] A.B. Metzner, R.E. Otto, Agitation of non-Newtonian fluids, AIChE J. 3 (1957) 3–10.

[26] G. Delaplace, R. Guerin, J.C. Leuliet, R.P. Chhabra, An analytical model for the prediction of power consumption for shear-thinning fluids with helical ribbon and helical screw ribbon impellers, Chem. Eng. Sci. 61 (2006) 3250–3259.