Effect of Hydrothermal Pretreatment of Corn Stover with pH Adjustment on Properties of Pulp and Hydrolysate

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In view of environmental and economic issues, co-production technology with pulp as the major product is an important developmental direction in biorefinery. In this paper, high-yield pulp was prepared by hydrothermal pretreatment with controlled pH and subsequent mechanical refining using corn stover as raw material. By adding acetic acid or sodium hydroxide, the properties of the hydrolysate and the pulp were altered. Reducing the pH during hydrothermal pretreatment resulted in more cellulose and hemicellulose being released, while less lignin was released. Increased pH led to more lignin being released, while dissolution of carbohydrates did not change significantly. A maximum pulp yield at pH 5.84 of hydrolysate was obtained when 3.0% sodium hydroxide was used. The strength of pulp is highly related to the removal of lignin during hydrothermal pretreatment. The relationship between pH value in hydrothermal pretreatment and the physical properties of the pulp was established and could be further used for prediction and as guidance for process control. Moreover, the results could be used to develop technologies for industrial utilization of agricultural straw to co-generate fiber and other bio-based products.

Keywords: Agricultural straw; Corn stover; Hydrothermal pretreatment; Pulp; Strength properties

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INTRODUCTION

Maize is widely cultivated in China. As an important biomass resource (de Souza *et al.* 2013), the total amount of available corn stover in China is approximately 216 million tons per year (Yang *et al.* 2019). Corn stover is composed of cellulose, hemicellulose, lignin, and a small amount of extractives and ash. It has been widely used as animal feed and has also been returned to the field or used for briquettes fuel, power generation, papermaking, *etc.* (Kim and Dale 2004). In recent years, corn stover has been utilized to produce bio-gas and nanostructured materials (Lin *et al.* 2019) in addition to ethanol (Taherdanak and Zilouei 2014).

Soda cooking and kraft cooking are commonly used chemical methods to manufacture pulp for papermaking. However, the spent liquor generated in the cooking process brings environmental issues. In comparison, hydrothermal pretreatment is an environmentally friendly process and causes little corrosion to equipment (Kim *et al.* 2009). In order to overcome the drawbacks of soda cooking and kraft cooking to manufacture pulp for papermaking, hydrothermal pretreatment was developed to produce fibers (Rolf *et al.* 2009). Compared with chemical pulp, the corn stover pulp obtained using hydrothermal pretreatment has a larger fiber length with higher yield. Moreover, the black liquor produced during chemical pulping is usually combusted for power generation (Cheng *et al.* 2010) while the hydrolysate produced via the hydrothermal method can be used to produce ethanol, hydrogen, and biogas (Leza 2011). Hydrothermal pretreatment is considered to be one of the most effective pretreatment methods to produce cellulosic ethanol from corn stover in terms of technology and economy (Imman *et al.* 2014; Wang *et al.* 2018).

Furthermore, the large amount of sugars in the hydrolysate could be applied in many areas. Xylose has been reported as beneficial for weight control and diabetes, and xylooligosaccharide was found to effectively reduce blood pressure (Park *et al.* 2001). Temperature and time are two important factors in the hydrothermal pretreatment process. A severity factor (SF) was generally used to evaluate the degree of pretreatment (Overend and Chornet 1987; Abatzoglou *et al.* 1992; Garrote *et al.* 2008; Ligero *et al.* 2011). Controlled pH hydrothermal pretreatment has also been studied in recent years. Li *et al.* (2014) found that when the severity factor was 4.0 and 2% (w/w) sodium hydroxide was added, the retention rate of hemicellulose was 96.4%. Jiang and Xu *et al.* (2016) treated corn stover using combined deacetylation and hydrothermal pretreatment and reported that when the amount of potassium hydroxide was 9% (w/w) and the severity factor (SF) of hydrothermal pretreatment was 3.97, the efficiency for further enzymatic hydrolysis reached 80% after 80 h. Whether it is acidic or alkaline, hydrothermal pretreatment increases the specific surface area of corn stover, which promotes the saccharification of corn stover to ethanol (Li *et al.* 2012; Zhao *et al.* 2012).

Integrating fiber into bioenergy production has been considered a promising method to address economic and environmental concerns. As shown in previous research, it is possible to produce pulp from corn stover through hydrothermal pretreatment and subsequent mechanical refining (Han *et al.* 2018; Zhang *et al.* 2019). However, the strength of produced pulp was low. Therefore, the aim of this work was to investigate the possibility of improving the mechanical properties of fibers by adjusting pH in hydrothermal pretreatment. In this paper, high-yield corn stover pulp was prepared by hydrothermal pretreatment with adjusted pH by adding acetic acid or sodium hydroxide. Meanwhile, the chemical composition of hydrolysate obtained at different pH values was analyzed so as to lay a foundation for further bio-based products application.

EXPERIMENTAL

Raw Material

Corn stover was collected from Dezhou, Shandong Province, China. The corn stover was air-dried and the aerial portion (all parts except for the root) was cut into pieces 2 to 4 cm in length, then thoroughly sieved to remove other impurities. The obtained raw material was stored at 4 °C.

Hydrothermal Pretreatment Process

A total of 300 g of prepared raw materials and 1500 mL of deionized water along with a certain proportion of acetic acid or sodium hydroxide (as listed in Table 1) was added to the batch electric heating rotary digester for hydrothermal pretreatment (KRK, Tokyo, Japan). Upon completion, the slurry was removed, and the liquid residual was separated from the solid residual using a nylon bag with 400 mesh. The pH value of the liquid fraction was measured using a pH meter. The solid residual was washed three times with 5000 mL of deionized water and stored in a sealed polyethylene plastic bag at 4 °C.

The liquid fraction together with washing water was collected for further analysis.

Table 1. Hydrothermal Pretreatment Conditions[a]

Experiment No.	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**
Acetic acid dosage (%)[b]	4.00	3.00	2.00	1.00	0	0	0	0	0	0	0	0	0
Sodium hydroxide dosage (%)[b]	0	0	0	0	0	1.00	2.00	3.00	4.00	4.25	4.50	4.75	5.00

[a]: solid to liquid ratio was 1:5 and severity factor was 3.77
[b]: Relative to oven-dried raw materials

The severity factor (SF) was used to indicate the cumulative effect of temperature and time in the cooking process. The severity factor (Overend and Chornet 1987) was calculated by a combination of empirical formulas as follows,

$$\mathrm{SF}=\log_{10}[R]=\log_{10}[t\cdot e^{\frac{T-T\mathrm{ref}}{14.75}}] \quad (1)$$

where t is reaction time (min), T is reaction temperature (°C), and T_{ref} is the reference temperature (°C), which is 100 °C in this experiment. In the process of heating and cooling, this paper used 5 min as an interval after the temperature exceeded 100 °C, and the calculation was as follows,

$$\mathrm{SF}=\log_{10}[R]=\log_{10}\left[\sum_{t_{T>100℃}}^{t_{\mathrm{end}}} R(t)\cdot\triangle t_{5\mathrm{min}}\right] \quad (2)$$

where t_{end} is the end of hydrothermal pretreatment process and $t_{T>100^\circ\mathrm{C}}$ is the point when reaction temperature exceeded 100° C.

Refining

The solid residual was refined by using a high consistency disc refiner (KRK, Tokyo, Japan) at a concentration of 20% and a disk gap of 0.15 mm. The obtained pulp was collected and stored at 4 °C.

Determination of Sugars and Fermentation Inhibitors

The concentration of monosaccharides (glucose, xylose, and arabinose) and fermentation inhibitors [5-hydroxymethylfurfural (5-HMF), furfural, acetic acid, and levulinic acid] in the hydrolysate and washing water was analyzed after centrifugation and filtered through a microporous membrane (0.22 um) using high performance liquid chromatography (Agilent 1200, Santa Clara, CA, USA). The measurement was performed with an Aminex HPX-87H column (Bio-Rad, Hercules, CA, USA) at 55 °C with 0.005 M H_2SO_4 as the mobile phase at a rate of 0.6 mL/min. The content of dissolved lignin in hydrolysate was determined by UV spectrophotometry at 225 nm, with distilled water as a reference (Lee *et al.* 2013). The total sugar concentration in the hydrolysate and washing water was determined after the sample was centrifuged and then hydrolyzed using 4% sulfuric acid at 121 °C for 60 min.

The chemical compositions of the raw material were determined according to the standard provided by the National Renewable Energy Laboratory (NREL), specifically including cellulose, xylan, arabinan, lignin, and ash (Sluiter *et al.* 2008).

Handsheet Preparation and Determination of Physical Properties

The handsheets with a basis weight of 100 g/m^2 were prepared using a rapid paper sheet former (RK3A-KWT, PTI, Vorchdorf, Austria) and dried under a vacuum degree of -90 kPa at 95 °C for 5 min. The prepared handsheets were treated at 23 °C and a relative humidity of 50% for more than 4 hours before testing. The basis weight, thickness, tensile strength, bursting strength, and ring crush strength of the handsheet were determined according to GB/T451.2 (2002), GB/T451.3 (2002), GB/T453 (2002), GB/T454 (2002), and GB/T2679.8 (1995), respectively.

RESULTS AND DISCUSSION

Solid Yield and pH of Hydrolysate after Hydrothermal Pretreatment under Different Acid and Alkali Intensities

The chemical composition of the corn stover is shown in Tab. 2. It shows that the contents of cellulose and hemicellulose in the raw materials were 38.7% and 22.9% respectively, and the content of lignin in the raw materials was 19.6%, of which acid-soluble lignin accounted for 2.2% of the total lignin. Table 2 additionally shows that the ash content of the corn stover was relatively higher, which likely affected the recovery of the hydrolysate. The flow chart in this study is illustrated in Fig. 1.

Table 2. Chemical Composition Analysis of Corn Stovers[a]

Cellulose (%)	Hemicellulose[b] (%)	Klason Lignin (%)	Acid Soluble Lignin (%)	Total Lignin (%)	Ash (%)
38.7 ± 0.24	22.9 ± 0.18	17.4 ± 0.15	2.2 ± 0.09	19.6 ± 0.24	10.5 ± 0.14

[a]:Results based on 100 g of oven-dried original raw material. The range and average of duplicate measurements is reported
[b]:The sum of xylan and arabinan

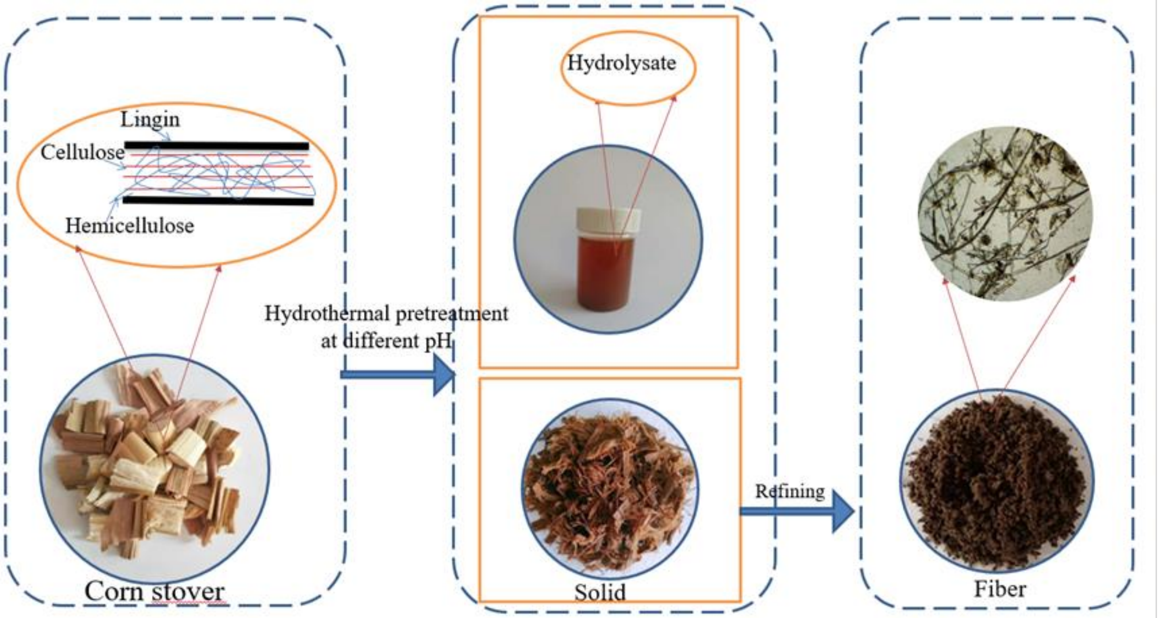

Fig. 1. The flow chart in this study

Table 3 shows that the pH value of the hydrolysate was 4.72 when only water without any chemicals was utilized in hydrothermal pretreatment. The pH value of the hydrolysate decreased slowly as the added amount of acetic acid increased, while the pH value of the hydrolysate increased rapidly as the added amount of sodium hydroxide increased. The pH value of the hydrolysate can reflect the change of acid and alkali intensities in hydrothermal pretreatment and it can be used as an indicator to reflect the pH value in hydrothermal pretreatment process.

Table 3. Solid Yield and pH of Hydrolysate after Hydrothermal Pretreatment under Different Acid and Alkali Intensities

Experiment No.	Pulp Yield (%)	pH of Hydrolysate
a	60.86	4.23
b	61.60	4.35
c	61.87	4.47
d	61.99	4.57
e	64.36	4.72
f	67.87	5.12
g	73.45	5.51
h	75.15	5.84
i	65.13	6.33
j	64.98	6.65
k	64.58	6.86
l	63.44	7.96
m	61.23	8.38

Due to the addition of acid or alkali in hydrothermal pretreatment, the pH value of the hydrolysate changed, which resulted in a change in the solid substance yield. With the increase in pH value of the hydrolysate, the yield of solid substances first increased and then decreased. It reached a maximum value at pH 5.84, which may be related to the degradation rate of the main chemical components in corn stover under different pH values.

Effect of pH Value on Major Chemical Components in Hydrolysate during Hydrothermal Pretreatment

Hemicellulose-related components

Hemicellulose in corn stover is mainly composed of xylose linked by (1,4) β-glycosylation as the backbone. The side chain of hemicellulose is composed of arabinose, glucuronic acid, galacturonic acid, acetyl and methoxy groups (Sidiras *et al.* 2011). Under liquid hot water pretreatment, some hemicelluloses are degraded to xylose, arabinose and acetyl (Laser *et al.* 2002; de Jong *et al.* 2012; Li and Xu 2013; Li *et al.* 2014). As shown in Fig. 2a, for pH values below 5.84, the amount of sugars, mainly composed of xylose, arabinose and xylooligosaccharide, in the hydrolysate increased from 4.37% (relative to oven-dried raw materials) to 8.38% as the pH value decreased. When the pH was higher than 5.84, the amount of sugars increased slightly from 4.37% to 6.78% as pH increased. Hydrochloric acid has been reported to increase solubilization of the hemicellulose fraction in hydrothermal pretreatment method by other researchers (Imman *et al.* 2014). In this study it was found that adding acid in hydrothermal pretreatment can greatly increase the content of sugars in hydrolysate.

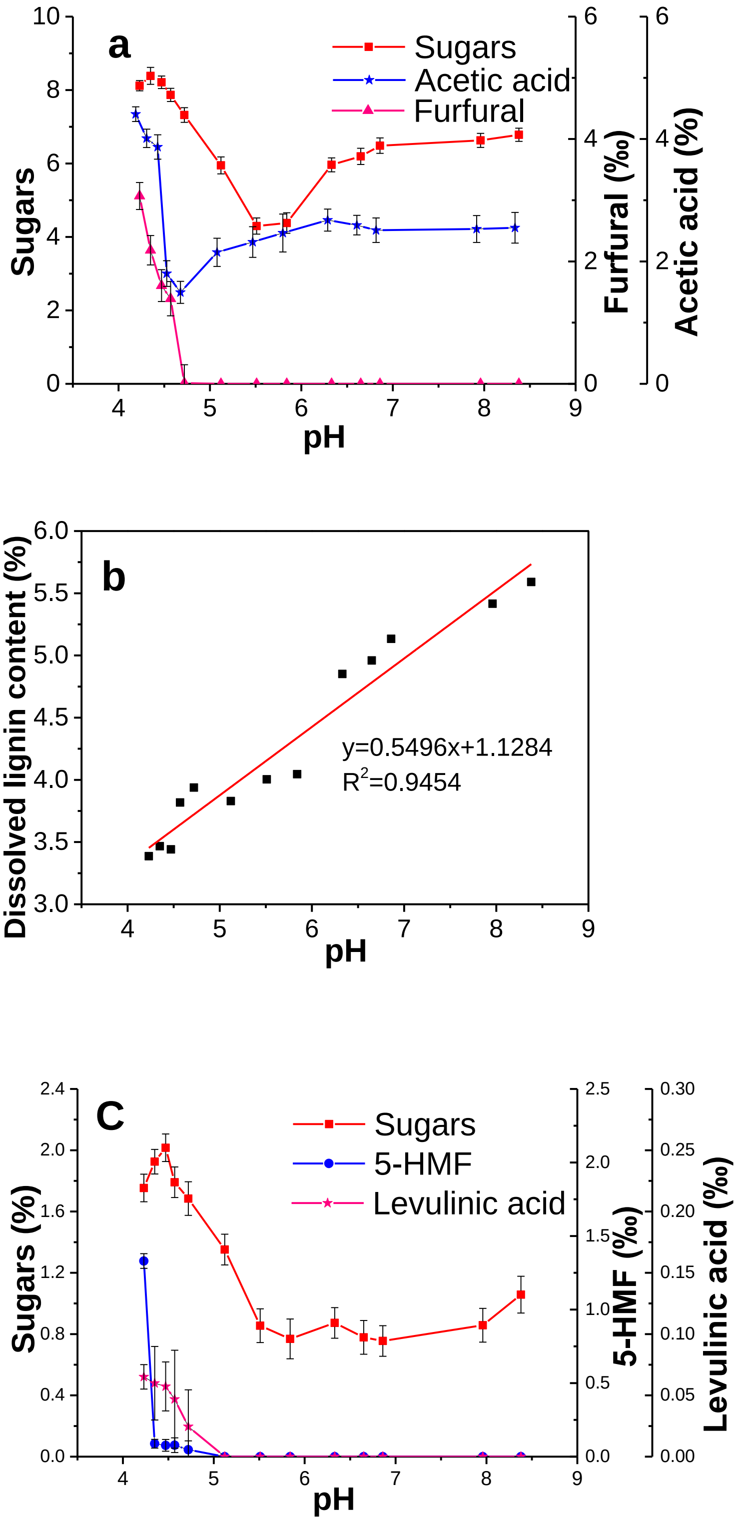

Fig. 2. Dissolution of hemicellulose-related components (a), lignin (b), and cellulose-related components (c) after hydrothermal pretreatment under different pH

Acetyl groups in hemicellulose can be easily removed, leading to the formation of acetic acid (Lora and Wayman 1978; Stuhler 2002), and the acetyl ester bond is easier to hydrolyze than the glycoside bond under acidic or alkaline conditions. It was observed that the amount of acetic acid in the hydrolysate was the lowest when neither alkali nor acid was added in hydrothermal pretreatment. For experimental groups e to a, acetic acid in the hydrolysate came from addition in the pretreatment process together with abscission of acetyl groups from hemicellulose in acidic conditions. Moreover, for experimental groups e to m, the amount of acetic acid removed first increased and then leveled off with increased addition of sodium hydroxide. When the amount of sodium hydroxide is less than 3%, sodium hydroxide is mainly consumed in the removal of acetyl groups. Pentose in the hydrolysate is converted to furfural when the pH value is low. Therefore, with the increase of acetic acid dosage, the furfural content in the hydrolysate increases. Singh *et al.* (2019) found that a higher dilute acid concentration resulted in a lower yield of pentose, indicating that the content of the pentose decreases when the amount of furfural in the hydrolysate increases. There was no furfural detectable in the hydrolysate when the pH value was above 5.12.

The amount of hemicellulose-related degradation substances in the hydrolysate was the lowest at pH 5.84 over the experimental range, indicating that hemicellulose was the most stable under the condition, which was one of the reasons for the high yield of solid materials at pH 5.84. If pH was greater than or lower than this value, the degradation of hemicellulose increased, especially when pH was lower.

Lignin component

Lignin in corn stover consists of three types of phenylpropane in different positions. As shown in Fig. 2b, pH has a great influence on the removal of lignin from raw materials. It can be obviously observed that the lignin in hydrolysate increased linearly from 3.5% to 5.8%, as pH was raised from 4.23 to 8.38. The same results were also reported by Jiang and Xu *et al.* (2016) and Li *et al.* (2013). Under acidic conditions, unshared electrons on the lignin ether bond are attacked by acidic groups, resulting in the breaking of α-ether bonds and the partial disintegration of lignin (Hu *et al.* 2012; Huijgen *et al.* 2012; Wildschut *et al.* 2013). With the increase of acetic acid dosage, the removal rate of lignin decreased due to the occurrence of the lignin condensation reaction. With the increase of sodium hydroxide dosage, the removal rate of lignin increased. The content of lignin phenolic structures in corn stover is high and they can be easily removed under alkaline conditions. As shown in Fig. 2a and 2b, when the added amount of sodium hydroxide is less than 3%, sodium hydroxide is mainly consumed in the removal of acetyl. When the added amount of sodium hydroxide is more than this value, sodium hydroxide mainly promotes degradation and dissolution of lignin.

Cellulose-related components

With the removal of hemicellulose and lignin, more cellulose is exposed and broken under acidic conditions (Sun and Cheng 2002; Wong *et al.* 1988). Under acidic conditions, cellulose is degraded to glucose, which dehydrates to produce 5-hydroxymethylfurfural (5-HMF), and 5-HMF further decomposes into formic acid and levulinic acid (Rose *et al.* 2000; Hideno *et al.* 2013). As illustrated in Fig. 2c, when the pH dropped below 5.84, it was found that the level of sugars from cellulose rose sharply. Singh *et al.* (2019) considered that the inflection point in change of glucose concentration occurred with the increase of dilute acid concentration during dilute acid pretreatment. When the pH value increased above 5.84, the level of sugars from cellulose was found to be almost constant. Appropriate alkali concentration can inhibit the removal of cellulose from straw (Hendriks and Zeeman 2009). When the pH of the hydrolysate was less than 5.12, both 5-HMF and levulinic acid production began to rise, indicating that glucose began to degrade.

In sum, the addition of acid was more beneficial to the degradation of cellulose and hemicellulose, while the addition of alkali is more beneficial to the removal of lignin in hydrothermal pretreatment. The amount of cellulose and hemicellulose-related sugars in the hydrolysate was the lowest at pH 5.84 when the yield of solid substance after hydrothermal pretreatment was the highest.

Effect of pH Value on Pulp Properties during Hydrothermal Pretreatment

Figure 3 shows that hydrothermal pretreatment appeared to be destructive to the integrity of the biomass, resulting in smaller particle sizes compared to the raw material, but the process also left a number of larger particles intact. The pretreated corn stover samples were transformed from a dark-brown to a light yellow color with the change of pH from acidic to alkaline. With the increase of acetic acid dosage, lignin condensation resulted in a darker color of solid materials (Imman *et al.* 2014). The removal of more cellulose and hemicellulose resulted in more broken solid materials. With the increase of sodium hydroxide dosage, more lignin is removed, resulting in the brighter color of solid materials and the more easily dispersed fiber bundles.

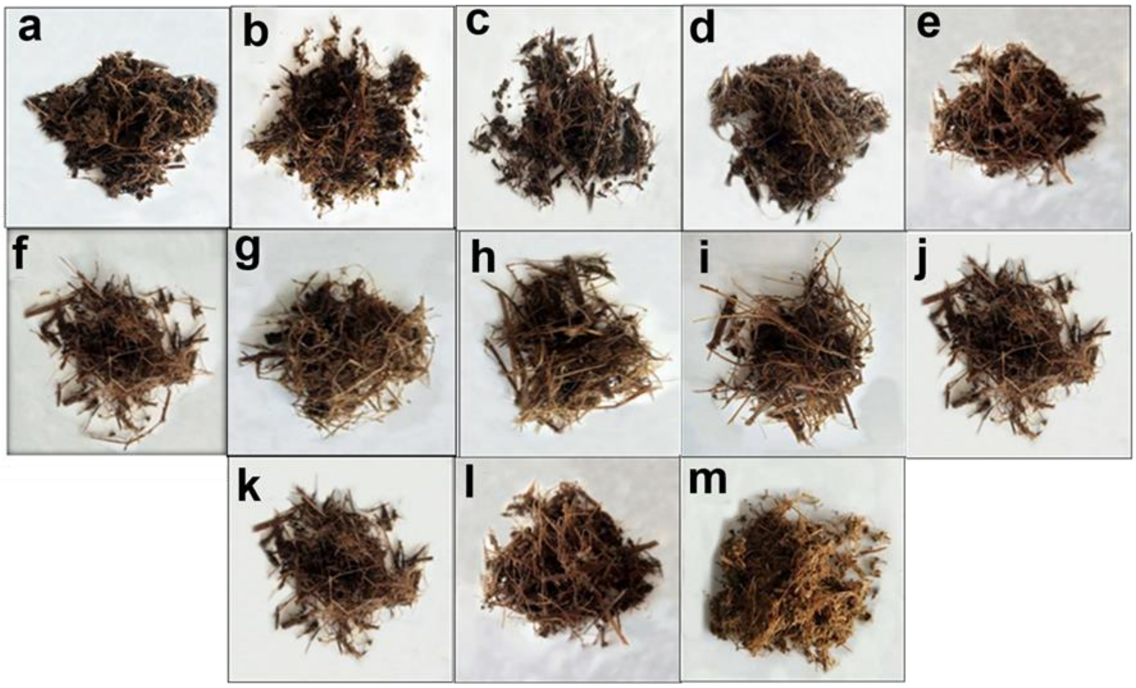

Fig. 3. Images of solid obtained after hydrothermal pretreatment under different pH

A further decrease in particle size was obtained with the disc refiner due to the grinding effect between the stationary disk and the rotating disk. The physical properties of the handsheet made from the obtained pulp were evaluated and the results are shown in Fig. 4. The non-linear regression analysis between the pH value in hydrothermal pretreatment and the properties of the handsheets was investigated, and the high coefficients of the fitting results indicated that they could be further used for property prediction over the pH range of 4.23 to 8.38.

Apparent density is one of the basic properties of paper. When the pH changed from 4.23 to 8.38, the apparent density of the handsheet was found to decrease from 0.5 g/cm3 to 0.42 g/cm^3, then increase to 0.62 g/cm^3. When the dosage of acetic acid increased, more fines were generated, which filled the gap between the fibers in the handsheet, resulting in a decrease in the strength of the handsheet and an increase in the density of the handsheet (Kinsley Jr 1989; Lei *et al.* 2013; Han *et al.* 2019). However, as alkali dosage was raised, fibers turned swollen and collapsed more easily as more lignin was removed, thereby increasing inter-fiber bonding (Bian *et al.* 2007; McIntosh and Vancov 2011; Zhao *et al.* 2012) and leading to the increased density of the paper.

Tensile strength, ring crush strength, and bursting strength are important quality requirements of packaging paper, including fluting base paper and linerboard. As shown in Fig. 4, the change in tensile index, ring crush index, and bursting index exhibited similar tendencies within the pH range studied.

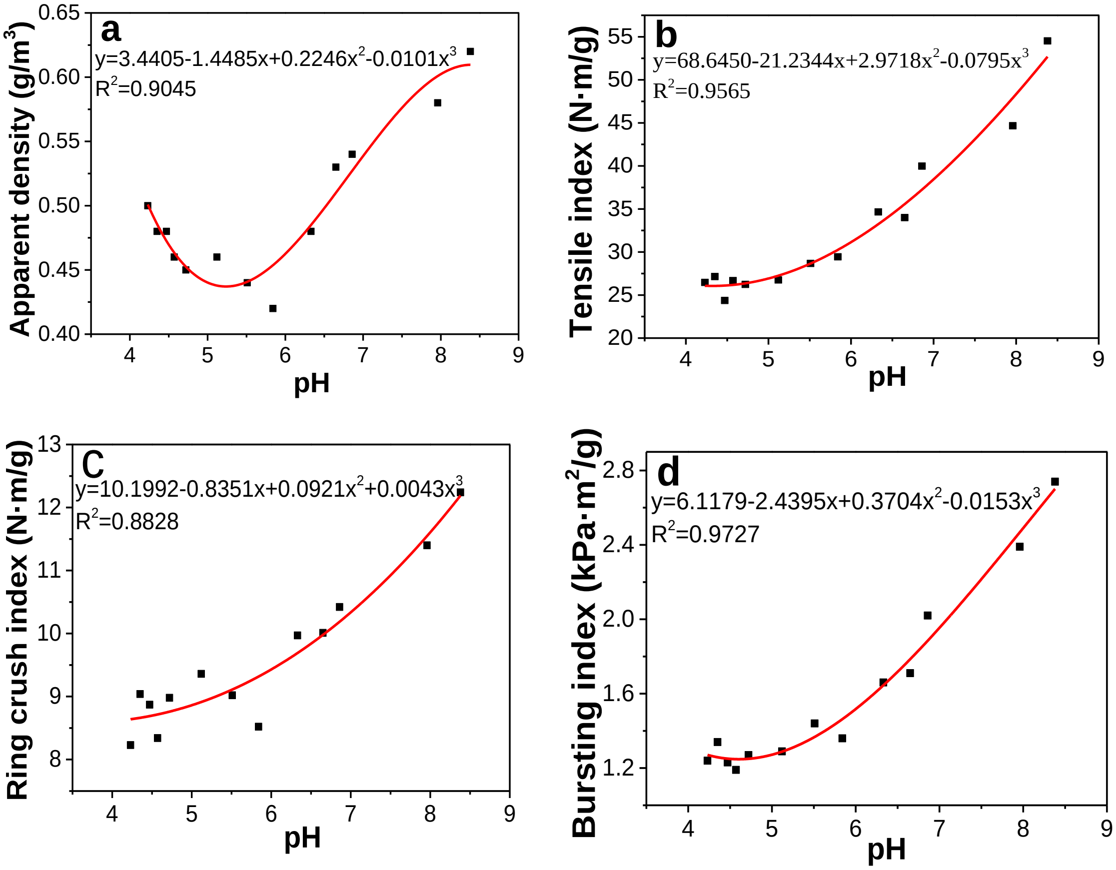

Fig. 4. Effect of pH value on pulp properties during hydrothermal pretreatment

With the increase in pH, the tensile strength, ring crush strength, and bursting strength of the obtained handsheet increased. The tensile index increased from 26.5 N•m/g to 54.5 N•m/g, and the ring crush index increased from 8.23 Nm/g to 12.24 Nm/g. Similarly, the bursting index increased from 1.24 kPa•m^2/g to 2.74 kPa•m^2/g. The influence of pH on the strength of the handsheet can be divided into two stages. The first stage is when the pH is less than 5.81 corresponding to an amount of sodium hydroxide less than 3%, during which the strength of handsheet slightly increases with an increase in pH. The second stage is when the amount of sodium hydroxide is more than 3%, during which the strength of handsheet increases rapidly with the increase in pH.

Although the pulp properties obtained at low pH were relatively poor, it was still better than the recycled paper used to manufacture fluting base paper in China (Han *et al.* 2018). Therefore, it is a good substitute for the recycled waste paper. At this point, more hemicellulose- and cellulose-related degraded products remained in the hydrolysate and could be further utilized for bioenergy, bio-chemicals, and bio-materials production. Moreover, the properties of the pulp obtained at high pH value are better compared with that of the corn stalk pulp by traditional chemical method. Tschirner *et al.* (2007) made corn stalk pulp by traditional chemical method, whose tensile index and bursting index were 45.3 N• m/g and 3.8 kPa•m^2/g, respectively. Besides, the pulp yield was low**.** Therefore, the results in this work could be potentially used to develop technologies for co-generation of fiber and other bio-based products.

Figure 5 shows that the tensile strength of the handsheet exhibited very high relevance for lignin removal. When the removal rate of lignin exceeds a certain value, for example 4.5% in this study, the tensile strength of the handsheet increases rapidly, but when it is less than this value, the increase in handsheet strength is not remarkable. Removal of lignin rendered the fibers more flexible and facilitated the bonding between fibers (Bian *et al.* 2007). This shows that delignification is also important to increasing the strength of the handsheet during hydrothermal pretreatment, as in traditional pulping methods.

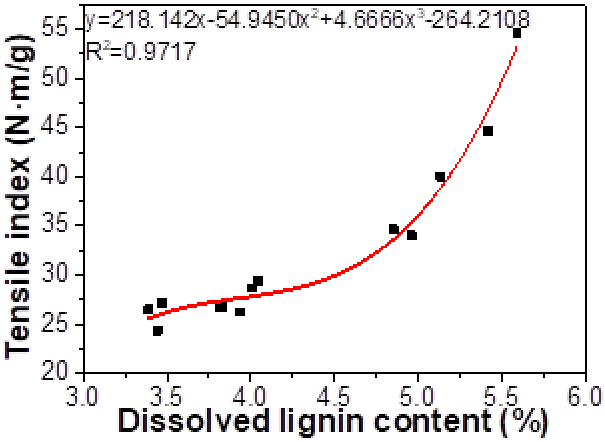

Fig. 5. Relationship between lignin removal and tensile index

CONCLUSIONS

1. Pulp with adequate properties for packaging was produced from agricultural straw by hydrothermal pretreatment and subsequent mechanical refining.
2. Acetic acid or sodium hydroxide in hydrothermal pretreatment can change the yield of solid materials as well as the pH value and composition of the hydrolysate. Increased acetic acid dosage caused more cellulose and hemicellulose to be released and less

lignin to be released. Increased sodium hydroxide dosage caused more lignin to be released while dissolution of carbohydrates did not change significantly.

3. The pH value had a great influence on the physical properties of the pulp, and the results in this work provided guidance to produce pulp with controlled properties through hydrothermal pretreatment. A maximum pulp yield at pH 5.84 of hydrolysate was obtained when 3% sodium hydroxide was added in hydrothermal pretreatment.
4. The produced high yield pulp can be used for fluting base paper, linerboard, and other products, which helps to solve the problem of shortage of fiber, especially in China.

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