

# The Preparation of Soluble Cellouronic Acid Sodium Salt by 4-Acetamide-TEMPO Mediated Oxidation of Ultrasound-Pretreated Parenchyma Cellulose from Bagasse Pith

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(received December 8, 2013; accepted June 11, 2014)

The parenchyma cellulose isolated from bagasse pith was used as an alternative resource for preparation of water-soluble cellouronic acid sodium salt (CAS). The influence of ultrasound treatment on the cellulose was investigated for obtaining CAS by regioselective oxidization using 4-acetamide-TEMPO and NaClO with NaClO<sub>2</sub> as a primary oxidant in an aqueous buffer at pH 6.0. The yield, carboxylate content and polymerization degree (DP) of CAS were measured as a function of ultrasonic power, agitating time and cellulose consistency by an orthogonal test. The ultrasound-treated conditions were further improved by discussion of ultrasonic power, the most important factor influencing the yield and DP. An optimized CAS yield of 72.9% with DP value (DP<sub>v</sub>) of 212 was found when the ultrasonic strength is 550 W, agitating time is 3 h and cellulose consistency is 2.0%. The oxidation reactivity of cellulose was improved by ultrasonic irradiation, whereas no significant changes in crystallinity of cellulose were measured after ultrasonic treatment. Moreover, the ultrasound treatment has a greater effect on yielding CAS from parenchyma cellulose than from bagasse fibrous' one. The CAS was further characterized by Fourier transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM).

**Keywords:** ultrasonic pretreatment, bagasse pith, parenchyma cellulose, cellouronic acid sodium salt, 4-acetamide-TEMPO.

## 1. Introduction

The preparation of oxidized cellulose containing carboxyl groups is of special interest due to its useful medical applications, such as adhesion-prevention, antitumor, wound-healing, and immunostimulant (COSERI *et al.*, 2013). The various kinds of potential oxidizing reagents have been developed for cellulose modification. In recent years, the use of non-persistent and stable nitroxyl radicals as catalytically selective agents for the conversion of primary hydroxyl groups into carboxylic ones has become one of the most studied topics in the field of cellulose oxidization. The phthalimide N-oxyl (PINO) radical generated in situ from N-hydroxyphthalimide (NHPI) and an appropriate cocatalyst (i.e., lead tetraacetate, cerium (IV) ammonium nitrate, anthraquinone), is one of non-persistent nitroxyl radicals efficiently for cellulose ox-

idation. Several advantages of PINO-mediated oxidation involved in the selective oxidization of viscose fibers in the presence of PINO radical with low amount of NaClO and NaBr (COSERI *et al.*, 2009), the alternative method for oxidizing viscose fibers in bromide-free system (COSERI *et al.*, 2012), and the mild oxidation of cellulose fibers using molecular oxygen as ultimate oxidizing agent (BILIUTA *et al.*, 2011). Apart from PINO, several other nonpersistent free radicals in situ generated from their OH correspondents: N-hydroxybenzotriazole (HBT), violuric acid (VA) and N-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI), have shown their effectiveness for the selective cellulose oxidation at pH 10 and room temperature in the presence of dilute solution of NaClO and NaBr (BILIUTA *et al.*, 2010).

Among the different kinds of catalysts reported in the literature, water-soluble and stable 2,2,6,6-

tetramethylpyperidine-1-oxy radical (TEMPO) or its derivatives (i.e., 4-acetamide-TEMPO) is another catalyst having the outstanding performance in cellulose oxidation (COSERI *et al.*, 2013; IWAMOTO *et al.*, 2010). In previous studies (REINA *et al.*, 2012; HIROTA *et al.*, 2009), the 4-acetamide-TEMPO-mediated oxidation could proceed under neutral or weakly acidic conditions, which avoid the depolymerization of cellulose chains by  $\beta$ -elimination of glycoside bonds at the C6 aldehyde groups formed as intermediate structures during oxidation at pH 9–11 (SHINODA *et al.*, 2012). Therefore, the oxidation system with catalytic amounts of 4-acetamide-TEMPO and NaClO applying NaClO<sub>2</sub> as the primary oxidant is more suitable than using TEMPO as catalyst at alkaline condition for preparation of water-soluble  $\beta$ -(1 $\rightarrow$ 4)-linked celouronic acid sodium salt with higher polymerization degree and yields.

As a rising interest in the new polyelectrolyte based on bio-polymers, the research of the oxidized cellulose is paid more attention to the CAS. In the case of the TEMPO-catalyzed oxidation of celluloses, water-soluble products are obtained, usually depending on the regenerated and mercerized celluloses in dried or never-dried state (BILIUTA *et al.*, 2013; ZHANG *et al.*, 2012). However, the celluloses reported in the scientific literatures are all isolated from pulp fibers of different raw materials but not yet from parenchyma cells.

Bagasse pith (BP) known as the agriculture residue of depithing bagasse, is usually used as the complementary boiler fuel in cane mill as well as bagasse pulp mill because of the dominant unavailable parenchyma cells in BP. It is a fact that the annual output of about 60 million ton of BP should not be reckoned with in natural resources. Based on the substantial amounts of polysaccharides contained in BP, its application should become more valuable than the simple burning. Generally, parenchyma cellulose has a much more loose structure than fiber's (YU *et al.*, 2008), indicating that cellulose from pith parenchyma cells has the comparatively more incompact super-molecular structure, and thus leads its optimism reactive properties for further derivative modification.

The ultrasonic agitation has been accepted as a promising useful and green method in cellulose modification by potentially changing structural and functional properties of irradiated cellulose (TANG *et al.*, 2005; LIU *et al.*, 2008). The ultrasound function including cavitation, heating, dynamic agitation, shear stresses and turbulence contribute to the improving of accessibility and reactivity of cellulose (VILKHU *et al.*, 2008; JAMBRAC *et al.*, 2009; CHEN *et al.*, 2011a). However, the literatures about CAS obtained from native celluloses were limited, and the combined effects of ultrasonic irradiation and 4-acetamide-TEMPO-mediated oxidation of parenchyma cellulose have not yet been reported.

The present study was to investigate the effect of ultrasonic irradiation on BP parenchyma cellulose, so as to further oxidize in 4-acetamide-TEMPO/NaClO/NaClO<sub>2</sub> system for producing CAS. Through revealing ultrasonic action on this system, it was hoped that the yield and polymerization degree of the CAS could be improved clearly.

## 2. Experimental

### 2.1. Materials

The parenchyma celluloses isolated from bagasse pith by the previous experiment intergraded with firstly oxygen treatment and secondly peroxide treatment with oxygen and anthraquinone as a catalyst were used as starting materials. The 4-acetamide-TEMPO, sodium chlorite, 10% sodium hypochlorite solution, and other chemicals and solvents were laboratory grade (Tokyo Chemical industry, Japan, or Aladdin, China), used without further purification.

### 2.2. Preparation of ultrasound-treated parenchyma cellulose and its CAS

Parenchyma cellulose pre-dried in the vacuum was soaked in 8 wt% NaOH solution with vigorous stirring for 1h at room temperature and then placed in a refrigerator at  $-20^{\circ}\text{C}$  overnight. The frozen cellulose was thawed and washed with water until salt-free, then separated from water by centrifugation. A scheme for oxidization of swollen cellulose pretreated by high-intensity ultrasonication was described below (shown in Fig. 1).

#### 2.2.1. Ultrasound treatment

Parenchyma celluloses were dispersed in certain amounts of distilled water, being the suspension slurries of different consistencies (1.0–2.5%). The ultrasound treatments of cellulosic slurries were carried out under the conditions of 300–900 W powers for 1–4 h in an ice bath, and performed in a way of treating 10 s with cooling intervals of 10 s by JY92-IIID type disrupter (manufactured by Ningbo Xin Zhi Sci and Equip Institute, 20 kHz frequency). Thereafter, treated cellulose was separated from water by centrifugation.

#### 2.2.2. Oxidation of parenchyma cellulose and isolation of soluble oxidized samples

The treated cellulose was suspended in acetate buffer dissolving 4-acetamide-TEMPO and sodium chlorite in a three-necked flask. The sodium hypochlorite solution was diluted with distilled water and added to the suspension. The flask was immediately stoppered and the mixture was stirred at  $40^{\circ}\text{C}$  for 1 day. Then another sodium chlorite and 1% diluted sodium

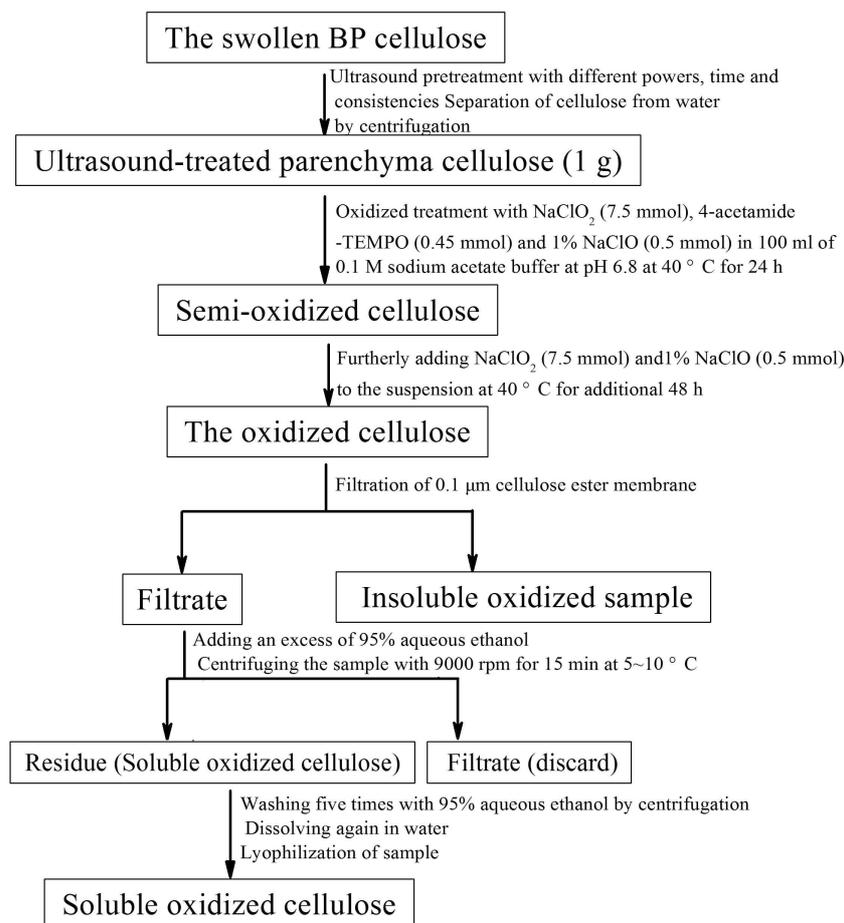


Fig. 1. Scheme for obtaining CAS by oxidation of ultrasound-pretreated cellulose from bagasse pith.

hypochlorite solution were further added to flask for 2 days at 40°C. After the oxidation, the water-soluble product was filtrated from insoluble part through 0.1 μm cellulose ester membrane (HIROTA *et al.*, 2009). The filtrate was precipitated by excessive ethanol addition. The precipitates were collected and washed with 95% aqueous ethanol by centrifugation. The soluble oxidized cellulose was dissolved again in distilled water and lyophilized.

### 2.3. Analyses

The yield of CAS was calculated according to:

$$\text{Yield (\%)} = (m_{\text{CAS}}/m_{\text{UTC}}) \times 100\%, \quad (1)$$

where  $m_{\text{CAS}}$  and  $m_{\text{UTC}}$  are the weights of dried CAS and ultrasound-treated cellulose in g, respectively.

Carboxylate content of each oxidized cellulose sample was determined according to the hydroxylamine method (KUMAR, YANG, 2002). The viscosity average DP<sub>v</sub> of the oxidized celluloses was determined from their intrinsic viscosities  $[\eta]$  in 0.5 M cupriethylene diamine,  $[\eta] = 0.61(\text{DP}_v)^{1.11}$  (REINA *et al.*, 2012). The parenchyma cellulose and the well-dispersed representative samples were observed with a scanning electron

microscopy (SEM, XL30 ESEM-TMP, EDAX, Ltd.) on aluminum stubs and coated with a thin layer of palladium-gold alloy. The X-ray diffraction (XRD) patterns were recorded for the pellet samples converted from freeze-dried oxidized products using in an X-ray diffractometer (D/max-2200, Japan) of CuK  $\alpha$  radiation at 40 kV and 20 mA. Scattered radiation was detected in the range of  $2\theta = 10\text{--}50^\circ$ , at a scan rate of  $4^\circ/\text{min}$ . The extent of crystallinity ( $C_I\%$ ) was estimated on the basis of areas under crystalline and amorphous peaks after an appropriate baseline correction and the applying of a deconvolution technique through the use of the MDI JADE 5.0 software. Fourier transform infrared (FT-IR) spectra of the oxidized celluloses were recorded on a Nicolet 560 spectrophotometer in the range  $4000\text{--}400\text{ cm}^{-1}$  using a KBr disc containing 1% finely ground sample.

## 3. Results and discussion

### 3.1. Effect of ultrasound treatment on structure changes of parenchyma cellulose

Figure 2 shows the SEM micrographs of parenchyma cellulose and the treated cellulose by ultra-

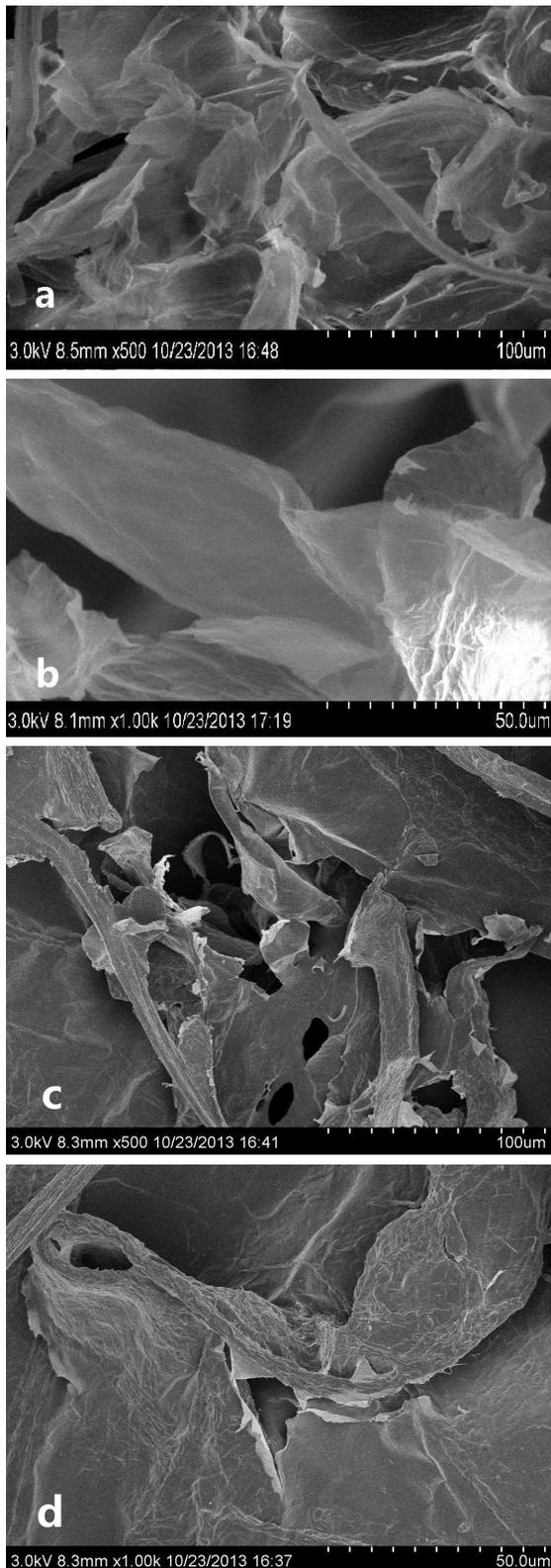


Fig. 2. SEM images of native parenchyma cellulose (a and b) and ultrasound-treated sample (c and d).

sonic irradiating at 550 W of power and 2.0% of cellulose consistency for 3 h. One can see the translucently flakiness-like shape that is the typical morphol-

ogy of parenchyma cellulose (Fig. 2a and b). After ultrasound treatment, the flakiness-like shape was still clearly observed, but the majority of parenchyma cells was cracked and fragmented into small flakes (Fig. 2c). A magnified image obviously shows the fibrillation in parenchyma cells (Fig. 2d). A similar phenomenon that the cellulose parenchyma changed its morphology under ultrasonic activation was reported for cellulose epidermal fibers (TANG *et al.*, 2005).

X-ray diffraction patterns of parenchyma cellulose and the treated samples at ultrasonic powers of 550 W and 900 W are depicted in Fig. 3. It can be seen that the crystallinities of parenchyma cellulose do not change so much after ultrasound treatment. There is no linear relationship between crystallinity and ultrasonic power.

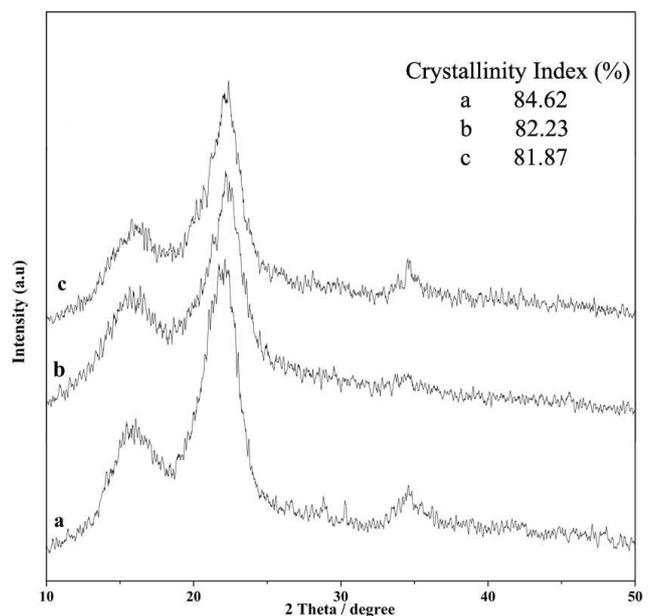


Fig. 3. X-ray diffraction patterns of parenchyma cellulose (a) and cellulose treated by ultrasonic power of 550 W (b) and 900 W (c) under conditions of 2.0% cellulose consistency for 3 h.

Combined with the analysis of SEM and XRD, it can be concluded that cavitation, which results from suddenly collapse of bubbles in the liquid medium by ultrasound waves (SUSLICK, 1990), effectively caused the morphological structure changes, but still had an insignificant impact on disrupting the hydrogen bonding of cellulose chains in the crystalline region of parenchyma cells.

### 3.2. Optimization of ultrasound-pretreated conditions on parenchyma cellulose for obtaining CAS

#### 3.2.1. Analysis of the orthogonal test results

Ultrasonic pretreatment of the BP cellulose was optimized for producing CAS with favorable properties

Table 1. The results from orthogonal test.

No.	Factors/Levels					Results		
	A, Ultrasonic power [W]	Empty column	B, Ultrasound treatment time [h]	Empty column	C, Cellulose consistency [%]	Yield [%]	Carboxylate content [%, w/w]	DP <sub>v</sub>
1	700 (A1)	1	3 (B1)	1	1.0 (C1)	75.2	35.44	161
2	700	2	4 (B2)	2	1.5 (C2)	73.5	35.74	160
3	700	3	2 (B3)	3	2.0 (C3)	77.0	36.04	165
4	700	4	1 (B4)	4	2.5 (C4)	68.7	35.47	159
5	300 (A2)	1	4	3	2.5	66.4	35.00	125
6	300	2	3	4	2.0	71.8	35.00	159
7	300	3	1	1	1.5	65.5	34.56	146
8	300	4	2	2	1.0	64.3	34.59	132
9	900 (A3)	1	2	4	1.5	65.4	35.78	159
10	900	2	1	3	1.0	66.6	35.51	156
11	900	3	3	2	2.5	66.0	36.00	174
12	900	4	4	1	2.0	69.4	35.43	180
13	500 (A4)	1	1	2	2.0	68.5	36.02	168
14	500	2	2	1	2.5	71.0	35.31	173
15	500	3	4	4	1.0	63.8	34.75	182
16	500	4	3	3	1.5	66.7	35.89	196

of the yield, carboxylate content and DP<sub>v</sub>. Ultrasonic power, treatment time and consistency were taken as major factors with 4 levels using orthogonal analysis. The experiment was carried out using an orthogonal L<sub>16</sub>(4)<sup>5</sup> test design. The 4 levels for each factor were arranged at random for maximizing data reliability (REN, 2003). The results of the orthogonal test are presented in Table 1 and the *R* values are shown in Table 2.

Table 2. *R* values of the three factors to the yield, carboxylate content and DP<sub>v</sub> of CAS.

<i>R</i> value	Yield [%]	Carboxylate content [%, w/w]	DP <sub>v</sub>
A	6.75	0.89	39
B	2.60	0.35	16
C	4.20	0.55	10

Although the 4-acetamide-TEMPO-mediate oxidation of cellulose has progressively proceed under neutral conditions, it is still difficult to avoid of substantial decreases in polymerization degree. Compared with the swollen parenchyma cellulose (486 of its DP<sub>v</sub>), the DP<sub>v</sub> of the CAS was decreased for all the factors at different levels. The lowest (141) DP<sub>v</sub> value of soluble oxidized fractions and the highest (180) after ultrasonic pretreatment were found for Factor A at Level A<sub>2</sub> (300 W) and Level A<sub>4</sub> (500 W), respectively. It is indicated that ultrasonic pretreatment had

a certain effect on accessibility of parenchyma cellulose in the next oxidizing process. According to the *R* values listed in Table 2, it can be found that the influence of these three factors studied on the DP<sub>v</sub> could be concluded to decrease in the order A > B > C. Apparently, Factor A (ultrasonic power) in the pretreatment process was the most important parameter to the DP<sub>v</sub>, which caused the maximum *R* value (39). Comparing the four levels chosen for each factor shown in Fig. 4a, the optimum conditions for a higher DP<sub>v</sub> were found to be A<sub>4</sub>B<sub>1</sub>C<sub>3</sub>, corresponding to 500 W ultrasonic power, 3 h reactive time and 2.0% cellulose consistency.

In addition, the effect of three ultrasonic factors with the four levels for each factor on the carboxylate content and yield of the oxidized products are shown in Fig. 4b and c, respectively. It can be seen that the best condition for both parameters was A<sub>1</sub>B<sub>1</sub>C<sub>3</sub>. And the maximum *R* values (also shown in Table 2) for carboxylate content and yield were both found to be Factor A, followed by C and B. Therefore, the 700 W was the favorable power strength for gaining highest yield and carboxylate content of CAS. However, there was a much less difference among three factors of the carboxylate content than those of the yield. Moreover, the maximum *R* was only 0.89 for carboxylate content, while it was 6.75 for the yield. These indicate that ultrasound pretreatment of parenchyma cellulose had a less effect on the content of carboxylate groups in its CAS, probably due to the fact that the

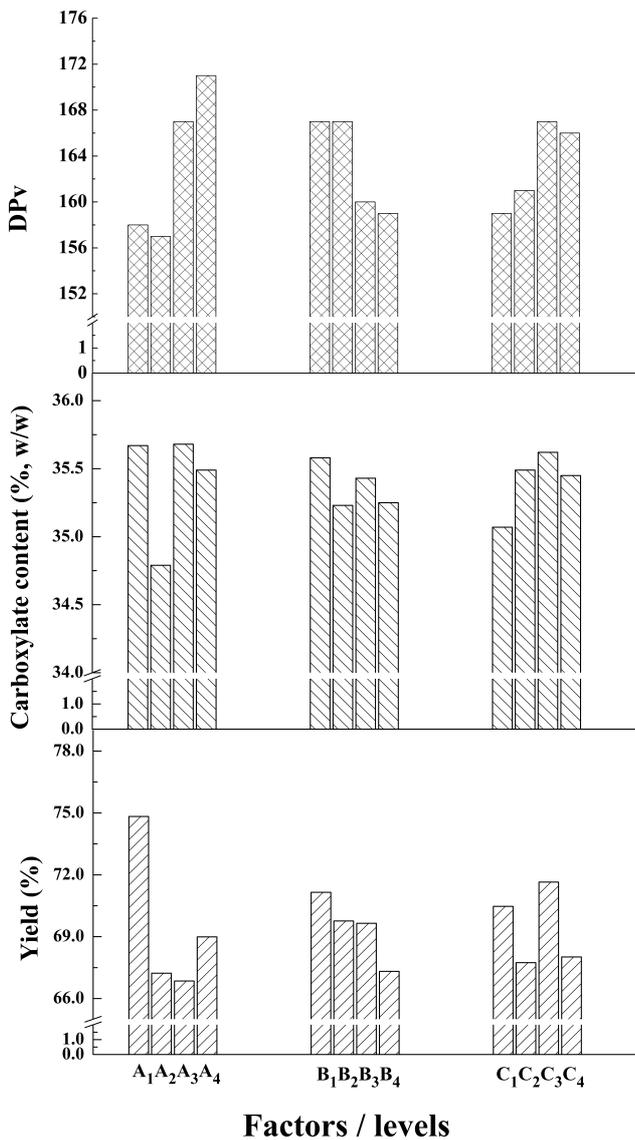


Fig. 4. The effect of the factors with different levels on CAS properties.

given conditions of the oxidation was enough sufficient to yield soluble fractions with high carboxylate content.

Based on the analysis above, ultrasonic power is the most significant factor affecting DPv and yield of CAS. However, the difference of each optimal condition for obtaining CAS of either high DPv or high yield was mainly focused on the ultrasonic strength. Hence, further study on the effect of ultrasonic power on balance of the two properties is necessary in order to find the optimal pretreatment conditions for oxidation of parenchyma cellulose.

### 3.2.2. Verification of ultrasound-power effect on CAS properties

The effect of ultrasonic power on DPv and yield of CAS is shown in Fig. 5. It can be seen that the

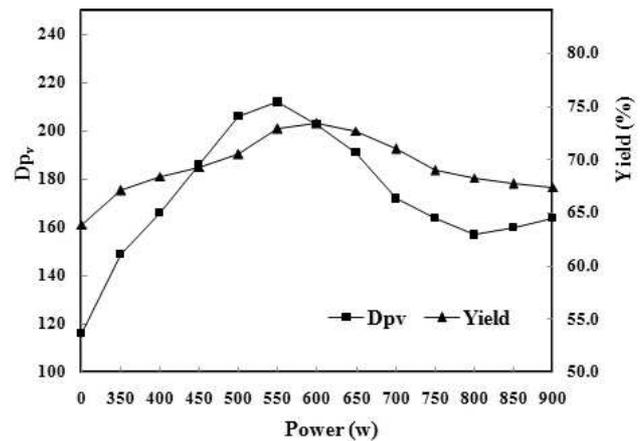


Fig. 5. The effect of ultrasonic power on DPv and yield of CAS.

polymerization degree values were increased with the powers enhancing from 350 W to 550 W. While further increasing the ultrasonic strength to 900 W appeared opposite phenomena. Hence, the optimal DPv values of CAS were 206, 212 and 203 corresponding to the powers of 500 W, 550 W and 600 W, respectively. Similar variation tendency of the yield with the ultrasonic powers can be also seen from Fig. 5, the ideal values of 72.9%, 73.4%, and 72.7% corresponding to the 550 W, 600 W and 650 W, respectively.

Under the same oxidation conditions, the DPv and yield of ultrasound-treated cellulose sample are both much higher than these of untreated parenchyma cellulose. It indicates that ultrasonic pretreatment has a great influence on the intrinsic structures of parenchyma cellulose, resulting in improving the accessibility (TANG *et al.*, 2005). So the reactivity of cellulose oxidized by the 4-acetamide-TEMPO/NaClO/NaClO<sub>2</sub> enhances as ultrasonic strength increases. Thus a larger quantity of oxidized cellulose particularly with higher molecules was formed and dissolved in aqueous system. However, the excessively increasing ultrasonic strength was detrimental to the polymerization degree and yield. So it indicates that the morphological structure changes such as over fibrillation, caused by ultrasound, significantly raises reactive behavior of treated cellulose, which was proved by the SEM images above. Consequently, the probability of oxidative degradation of cellulose, resulting from attack glycoside bonds of polysaccharides by active species formed in situ as by-products during the oxidation (SHIBATA, ISOGAI, 2003), was largely increased, which severely impaired the quality of CAS.

Taking into account of the energy consumption of ultrasonication, thereby the optimal pretreatment conditions of parenchyma cellulose for obtaining CAS can be concluded as 550 W ultrasonic power, 3 h reaction time, and 2.0% cellulose consistency.

### 3.3. Comparative CAS from ultrasound-treated fibrous and parenchyma cellulose

Comparatively, fibrous cellulose from depithed bagasse was chosen as a contrast material for obtaining CAS, which preparation was followed by the same process as the parenchyma cellulose. Under the optimized conditions of ultrasound pretreatment mentioned above, the oxidized product prepared from fibrous cellulose had yield (17.6%) much lower than those prepared from parenchyma cellulose (73.4%), even though both oxidized products had similar carboxylate contents (35.30% and 35.62% for fibrous and parenchyma celluloses, respectively) and DP values (220 and 212 for fibrous and parenchyma celluloses, respectively). Based on the results of comparative experiments (shown in Fig. 6), ultrasonic treatment of fibrous cellulose had less effect on its CAS yield than that of parenchyma cellulose. It was probably due to the parenchyma cellulose has a much more loose structure than fibrous part, that is, cellulose micro-structures, such as microfibrillar crystals, arrange randomly in the parenchyma cell walls but arrange quite orderly in the fibers, which may cause the parenchyma cellulose more vulnerable to ultrasonication for subsequently improving the regioselective oxidization. And the intrinsic structures of BP parenchyma cellulose for explaining its higher CAS yield will be thoroughly studied in the future research.

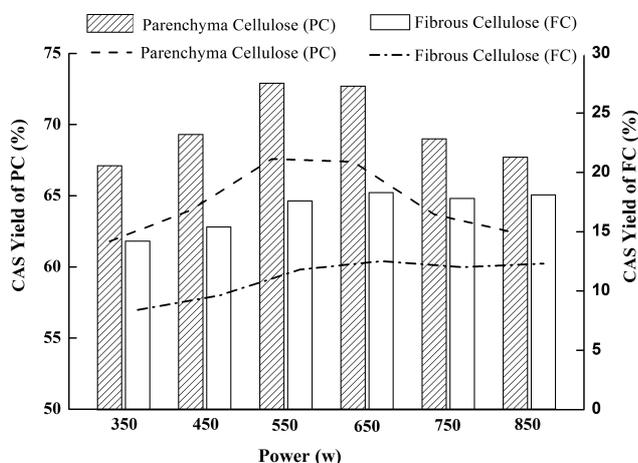


Fig. 6. The effect of ultrasonic power on yield of CAS obtained from parenchyma and fibrous celluloses.

### 3.4. FT-IR spectroscopy analysis

Figure 7 depicts the FT-IR spectra of parenchyma cellulose and CAS. Most of the bands ascribed to vibrations of cellulose backbone between 4000 and 800  $\text{cm}^{-1}$  are still visible, while the modifications of a few peaks and emergence of new bands are displayed in FT-IR spectra of CAS.

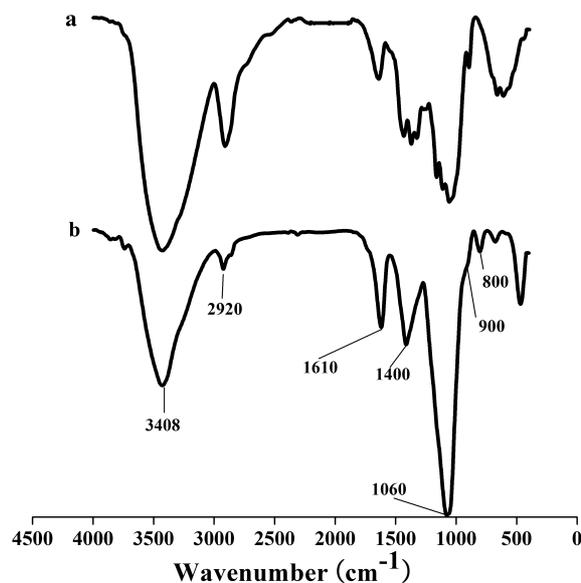


Fig. 7. FT-IR spectra of parenchyma cellulose (a) and CAS (b).

Because the peaks at 2920 and 1433  $\text{cm}^{-1}$  are attributed to C-H stretching and the bending of  $\text{CH}_2$  groups, respectively (CHEN *et al.*, 2011b), its intensities are decreased or even disappeared with the conversion of  $\text{CH}_2\text{OH}$  into carboxylate groups. Meanwhile, the intensity of a band at 900  $\text{cm}^{-1}$  related to  $\beta$ -glycosidic linkages between glucose units is also decreased, which is probably attributable to lower DPv of CAS than that of cellulose. The presence of a C-O-C skeletal vibrating band at 1060  $\text{cm}^{-1}$  provides evidence of glucopyranose ring structure of CAS. Moreover, new bands are notable at 1610, 1400 and 803  $\text{cm}^{-1}$ , which are ascribed to vibrations of  $\text{COO}^-$  groups (ZHANG *et al.*, 2012).

### 3.5. SEM analysis

The morphology of CAS samples from untreated and ultrasound treated cellulose was further investigated by SEM. As shown in Fig. 8, two kind CASs have a lamellar structure similar to that of native cellulose. However the size of oxidized cellulose seemed to become smaller (Fig. 8a and b) and the surface composed of micro-sized fibers was obviously rougher and more porous (Fig. 8c and d). In comparison with CAS from the untreated cellulose, the structure of CAS from the ultrasound-pretreated sample appeared to be more compact and ordered. This result indicated that the soluble oxidized particles with a higher DPv from ultrasound-treated cellulose was more likely to self-assemble microfiber-like structure by strong hydrogen bond of polar groups and therefore, form tight morphology during the drying process.

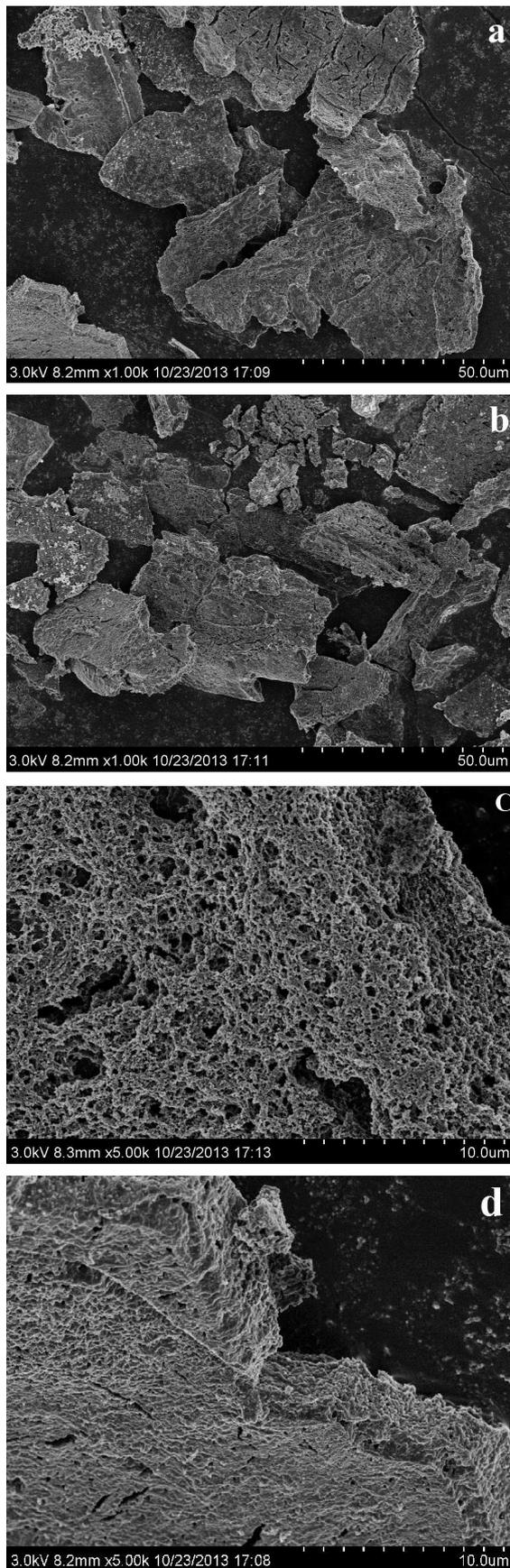


Fig. 8. SEM images of CAS prepared from cellulose without (a and c) and with (b and d) ultrasound irradiation.

#### 4. Conclusion

The morphological structure of cellulose has been changed by ultrasound wave, mainly reflecting both fibrillation and fragmentation, while crystallinity has not been greatly affected.

By ultrasound treatment the oxidation reactivity of cellulose in 4-acetamide-TEMPO/NaClO/NaClO<sub>2</sub> system is enhanced. Ultrasonic power was found to have the significant impact on the yield and DP<sub>v</sub> of CAS prepared from BP parenchyma cellulose, followed by the reaction time and cellulose consistency. The appropriate range of ultrasonic strength could promote the oxidation reactivity of cellulose, and the yield and DP<sub>v</sub> of CAS was found to become higher. The optimum conditions were ultrasonic power of 550 W, reaction time of 3 h, and cellulose consistency of 2.0%. CAS prepared under the above conditions had the yield of 72.9% and DP<sub>v</sub> value of 212. Moreover, the ultrasonication played a more apparent role in enhancing the yield of CAS prepared from parenchyma cellulose than that from bagasse fibrous cellulose.

FT-IR presents characteristic signals ascribed to the vibrations of carboxylate groups of oxidized samples. The result of SEM was revealed that CAS' surface was composed of micro-sized fibers, being rough and porous. In conclusion, ultrasound technique can be used as a potential efficient environmentally acceptable method for activating cellulose to prepare of CAS using relatively resourceful and inexpensive BP.

#### Acknowledgment

This research was supported by National Natural Science Foundations of China (21276119, 51363013), Scientific Research Foundation Project of Yunnan Municipal Education Commission (2012Y537) and Analysis Foundation of Kunming University of Science and Technology (20140853).

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