Effects of the Conditions of the TEMPO/NaBr/NaClO System on Carboxyl Groups, Degree of Polymerization, and Yield of the Oxidized Cellulose

Changmei Lin,[a] Tong Zeng,[a] Qinhua Wang,[a] Liulian Huang,[a] Yonghao Ni,[a,b]
Fang Huang,[a] Xiaojuan Ma,[a,]* and Shilin Cao [a,]*

Dissolving pulp from *Pinus caribaea* was oxidized by means of the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxide radical)/NaBr/NaClO system. Effects of the conditions including pH, NaClO dosage, and time on the carboxyl group content, degree of polymerization (DP), and solid recovery of oxidized cellulose were determined. A pH of 10 to 10.5 was found to be optimum for selectively oxidizing cellulose, and carboxyl groups were up to 0.75 mmol/g. However, increasing pH from 9 to 12 facilitated cellulose depolymerization by consistently indicating a gradual drop in DP, thus resulting in cellulose loss. In addition, oxidation was accelerated by the addition of 1 mmol/g to 6 mmol/g NaClO; however, further addition did not enhance the carboxyl groups. The maximum value of carboxyl groups was more dependent on NaClO dosage and governed by the crystal structure of the raw material. To obtain oxidized cellulose with a higher yield and DP, NaClO dosage could be controlled at 4 mmol/g to 6 mmol/g, while the reaction time was limited to 6 h to 8 h.

Keywords: Cellulose; TEMPO/NaBr/NaClO; Carboxyl groups; DP; Yield

Contact information: a: College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China; b: Limerick Pulp and Paper Centre, Department of Chemical Engineering, University of New Brunswick, Fredericton, E3B5A3, Canada;
** Corresponding authors: 1212juanjuan@163.com; scutcsl@163.com*

INTRODUCTION

As one of the cellulose derivatives, oxidized cellulose is widely used in hemostatic, film, filter, carbon aerogels, and textile material, among other applications (Wang *et al.* 2017; Wu and Cheng 2017; Abe *et al.* 2018; Lal and Mhaske 2018). In the past decades, many studies have been focused on oxidation of cellulose, with an objective to develop the material properties of cellulose by introduction of aldehyde and carboxyl groups (Kim *et al.* 2000; Saito *et al.* 2010). The catalytic oxidation method using stable nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was found to be one of the promising procedures for oxidation of cellulose; besides, NaBr and NaClO were used as catalyst and as a primary oxidant in conjunction with TEMPO (Habibi *et al.* 2006; Okita *et al.* 2010; Salminen *et al.* 2017).

The TEMPO mediated system is expected to catalyze the oxidation of primary alcohol groups to carboxyl groups in aqueous media; and it also has been applied in the preparation of nanofibrillated celluloses (Kuramae *et al.* 2014). In such applications, anionically charged functional groups are introduced onto the cellulose fiber surface to form strong electrostatic repulsion and therefore greatly enhance the ease of separation of individual microfibrils (Isogai *et al.* 2011). Specifically, the C6 primary hydroxyls of cellulose are selectively oxidized to become C6 carboxylated groups, and the oxidized products mostly have the homogeneous chemical structure of sodium (1→4)-β-D-polyglucuronate or Na salt of cellouronic acid consisting of D-glucuronosyl units alone (Saito *et al.* 2009; Isogai *et al.* 2011). However, remarkable depolymerization is inevitable in the TEMPO/NaBr/NaClO system under alkaline conditions. The degree of the polymerization of oxidized cellulose was far lower than that of the original cellulose (Saito and Isogai 2004; Funahashi *et al.* 2017; Sang *et al.* 2017). Of course, the methods used for DP determination might account for some of the sharp decrease; the presence of C6 aldehyde groups would initiate β-elimination in the copper ethylenediamine hydroxide solution and therefore result in a lower DP compared to the true value (Isogai *et al.* 2011).

As mentioned above, TEMPO can selectively oxidize primary hydroxyl groups of cellulose to carboxyl groups, and cellulose loss is inevitable. However, DP is one of the most important determinants for the strength, length, and flexibility of individual cellulose fibrils and has a direct relationship with the properties of their applications (Fukuzumi *et al.* 2013).

In the present work, the dissolving pulp prepared from pine wood was treated by TEMPO/NaBr/NaClO under various conditions. The focus was to investigate the effects of the conditions on the yield, DP, and carboxyl groups. The results are expected to help in the optimization of reaction conditions that are suitable for the subsequent application.

EXPERIMENTAL

Materials

Wood (*Pinus caribaea*) dissolving pulp was used as the original cellulose sample and was obtained from a local pulp mill (Fuzhou, China). The TEMPO (2,2,6,6-tetramethylpiperidine-1-oxide radical) was purchased from Aladdin (Shanghai, China). Sodium hypochlorite and sodium hydroxide were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Hydrochloric acid was obtained from Lanxi Xuri Chemical Co., Ltd. (Lanxi, China). Anhydrous ethanol, sodium bicarbonate, and sodium chloride were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Deionized water was made in the laboratory. The degree of polymerization of the starting cellulose sample was 480, while the carboxyl groups were not detected.

Methods

Cellulose oxidization

In the present work, the oxidized conditions of NaClO dosage, pH, and time were studied, while the NaBr and TEMPO were kept constant. The oxidation procedure generally followed the literature methods (Hirota *et al.* 2009; Shinoda *et al*. 2012; Fukuzumi *et al*. 2013; Gamelas *et al.* 2015). A total of 5 g pulp was dispersed in 500 mL deionized water and formed a 1 wt% pulp slurry. Next, 0.08 g TEMPO and 1 g NaBr were dissolved in 20 mL water and then added in sequence into the pulp slurry. The NaClO with different dosages (1 to 16 mmol/g dissolving pulp) was added drop-wise to the suspension to start the oxidation reaction. During the process, the pH of the reaction system was monitored and adjusted by uninterruptedly dropping NaOH solution within the range of 9 to 12. After a period of reaction (3 to 15 h), the reaction was quenched by adding excess ethanol (10 mL). Then, HCl (Hydrochloric acid) (1 mol/L) was used to adjust the pH of the solution at 7. The reaction product was filtered through a filter and washed thoroughly with ethanol and water until the Cl^- no longer was present in the filtrate. The ratio between the retained cellulose in the filter and the cellulose added was defined as solid recovery (yield, %).

Carboxyl group content determination

The carboxyl group content of TEMPO-oxidized cellulose was determined by headspace gas chromatography (Agilent 7890B, Germany) equipped with a headspace sampler (Thermo ScientificTM TriPlusTM 300, USA). The carboxylic acid group on TEMPO-oxidized cellulose reacts with sodium bicarbonate to produce CO_2 by acid treatment; the detailed procedure was described in previous studies (Chai *et al*. 2003; Li *et al*. 2015).

DP determination

The intrinsic viscosity of the oxidized cellulose samples was measured at 25 ºC with a capillary-tube viscometer (DP-02, Beijing hengchengyuke Co. Ltd, China) using cuproethylenediamine (CED) as the solvent, and these values were converted to viscosity average degree of polymerization (DP) by the reported method (Ma *et al.* 2013).

Fourier transform infrared (FTIR) spectra

Fourier transform infrared (FTIR) spectra of cellulose and TEMPO-oxidized cellulose were processed using a Thermo Electron Corporation Nicolet 380 spectrometer (VERTEX 70, Bruker, Germany). The sample was prepared by the KBr tableting method with a ratio of 1:100. The spectra were obtained *via* operating at a nominal resolution of 4 cm^{-1} and co-adding 100 scans in the region between 400 cm^{-1} and 4000 cm^{-1}.

X-ray diffraction (XRD)

The measurements of X-ray diffraction were operated on a high resolution X-ray diffractometer (Ultima IV, Japan). The patterns with Cu-Ka radiation (wavelength: 0.154 nm) at 40 kV and 40 mA were recorded in the region of 2θ =10° to 60° at a scanning rate of 5°/min and the step width of 0.02°. The crystallinity of the samples was determined based on the Segal method (Segal *et al.* 1959; French 2014).

RESULTS AND DISCUSSION

The Reagent Effects

The variables in the reaction system include concentrations of the reactants, pH, and the temperature. As described in the literature, the increase in the amount of TEMPO and NaBr sped up the reaction rate, but the carboxyl group content of TEMPO-oxidized cellulose was almost unchanged.

The NaBr and TEMPO are used only in catalytic amounts in the whole reaction process (de Nooy *et al.* 1996; Saito and Isogai 2004). In the present study, the temperature was kept constant in the whole experiment. Because temperature induces severe degradation effects (de Nooy *et al.* 1996; Sang *et al.* 2017), only the NaClO, pH, and time effects were investigated.

Table 1. Carboxyl Group Formation and Cellulose Degradation Changes with Various Reagents (pH 10.5, Reaction Time 6 h)

TEMPO (g)	NaBr (g)	NaClO Dosage (mmol/g)	Carboxyl (mmol/g)	Solid Recovery (%)	DP
0	0	0	Trace	99.6	479
1.6	0	0	Trace	99.6	460
0	1.0	0	Trace	99.6	454
0	0	4.5	Trace	96.5	379
1.6	1.0	4.5	0.73	90.8	122

Table 1 shows the effect of reagents on the carboxyl group formation and cellulose degradation. The TEMPO or NaBr applied alone barely induced a cellulose reaction, indicated by trace carboxyl group formation and invariable DP change. However, NaClO under alkaline medium degraded cellulose, which is shown by a lower DP (379 *vs.* 479); in fact, NaClO in alkaline is characteristic of a pulp bleaching system. It was reported that NaClO at pH 9 to 11 may cause the depolymerization of cellouronic acid (Shibata and Isogai 2003). Although cellulose cleavage occurred, carboxyl groups were not found in the cellulose after NaClO treatment without TEMPO and NaBr, as NaClO did not selectively oxidize the cellulose hydroxyl group of C6. However, treatment with the TEMPO/NaBr/NaClO system led to a remarkable carboxyl group formation and cellulose depolymerization. As compared between the different systems, only the TEMPO/NaBr/NaClO system selectively oxidized cellulose, while the NaClO in the alkaline medium had only some oxidizing effects on cellulose.

Figure 1 shows the FTIR spectra of the cellulose and oxidized cellulose. As well as cellulose, the oxidized cellulose showed a broad absorption around 3500 cm^{-1}, which can be ascribed to the stretching of H-bonded -OH groups; while the peak at 2900 cm^{-1} is due to C-H stretching.

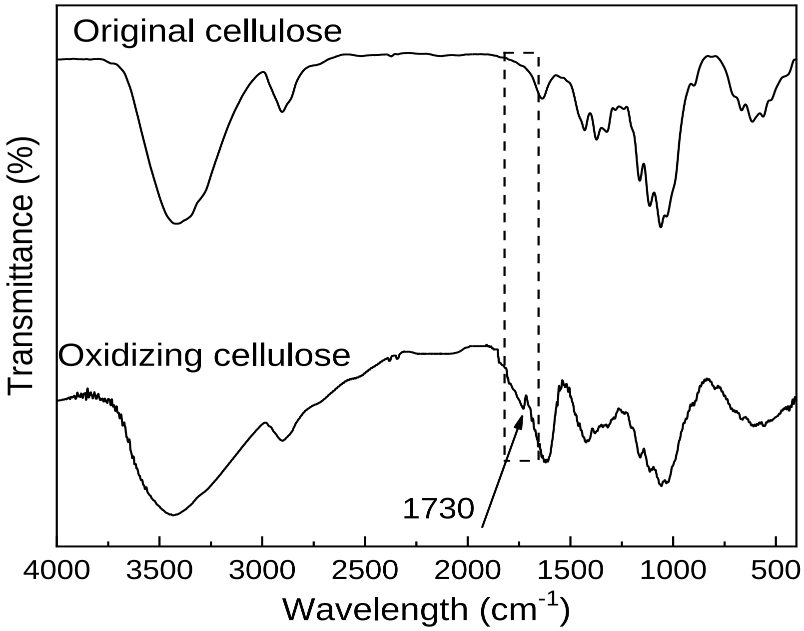

Fig. 1. FTIR spectra of cellulose and oxidized cellulose

The peak appearing at 1633 cm^{-1} in the two samples could be attributed to the bending mode of absorbed water in cellulose (Das *et al.* 2010). The 1429 cm^{-1} vibration could be assigned to CH_2 scissoring, while the 1376, 1317 and 1048 cm^{-1} vibrations were attributed to C-H bending, CH_2 rocking, and C-O stretching, respectively (Abidi *et al.* 2014).

Unlike original cellulose, the oxidized cellulose spectra showed a pronounced peak at 1734 cm^{-1}, which is attributed to the presence of carboxyl groups acquired during the TEMPO oxidation reaction (Poletto *et al.* 2014). The appearance of carboxyl groups indicated that the hydroxyl groups at the C6 position of the cellulose molecules were converted to carboxyl groups.

As compared between the different systems, only the TEMPO/NaBr/NaClO system selectively oxidized cellulose, while the NaClO in the alkaline medium had only some oxidizing effects on cellulose.

Effect of pH

Figure 2 shows the effects of pH on the oxidized cellulose. The carboxyl group formation had a strong correlation to pH. The carboxyl group content substantially increased from 0.45 mmol/g to 0.73 mmol/g as the pH varied from 9 to 10.5. With further increase of the pH to 12, the carboxyl content gradually declined. The pH governs the reaction mechanism and therefore affects the carboxyl formation. In contrast to findings that a higher oxidation rate was found at a pH 8 to 10 when the TEMPO/NaBr/NaClO system was used to oxidize an α-D-glucopyranoside sample (de Nooy *et al.* 1995), a higher oxidation rate was found at pH 10 to 10.5 when dissolving pulp cellulose was used.

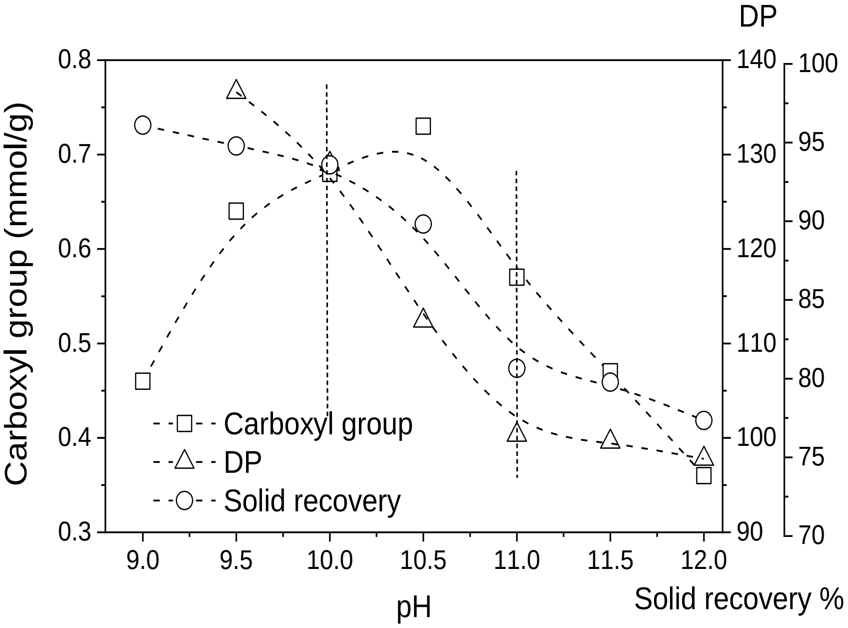

Fig. 2. The effects of pH on the oxidizing cellulose (NaClO 5 mmg/mol, time 6 h)

The hydroxyl radicals produced by TEMPO and NaClO lead cellulose to degrade during the oxidation process at pH 10 to 11 (Bragd *et al.* 2001; Shibata and Isogai 2003).

A study about the effects of pH on the depolymerization of cellouronic acid demonstrated that the system at pH 9 caused partial depolymerization of cellouronic acid; in this case, the DP decreased from 430 to 200 (DP almost leveled off) within the initial 30 min. Correspondingly, application of this system at pH 11 caused a severe degradation, in which the DP drastically decreased to 20 in the initial 10 min. Increasing the pH to a high level was favorable for cellouronic depolymerization. Similar effects were probably involved with cellulose degradation in the present system the authors studied. A gradual DP decrease and cellulose loss was observed with an increase of pH from 9.5 to 12, as can be seen from Fig. 2. Strictly, the DP slowly decreased when the pH was raised above 11; this agreed with the results from potato starch (de Dooy *et al.* 1995). Because of the mild degradation revealed from the lingering variation of DP, the solid recovery decreased slightly as well. However, the carboxyl groups declined consistently, indicating the decreased oxidation selectivity of the TEMPO/NaBr/NaClO system at this higher pH level. A pH of 10 to 10.5 proved most favorable for selective oxidation and protection of cellulose from severe degradation. Although pH higher than 10.5 had a comparable oxidation effect, the selectivity was decreased.

Effect of Sodium Hypochlorite Dosage

As shown in Fig. 3, a consistent increase of carboxyl content was observed with increased NaClO addition. Specifically, the carboxyl group formation was a function of NaClO dosage; as NaClO dosage ranged from 1 mmol/g to 6 mmol/g, the carboxyl groups increased substantially from 0.05 mmol/g to 1.09 mmol/g. Moreover, the relationship between NaClO dosage and carboxyl formation appeared linear. In contrast, when the NaClO dosage increased to 6 mmol/g and above, the carboxyl group content increased slowly and even remained stagnant, from 1.09 mmol/g to 1.38 mmol/g. The maximum value of carboxyl groups is more than two times that reported for cotton linter oxidized cellulose (Saito and Isogai 2004); however, it is comparable with that reported of kraft pulp (Saito et al. 2009; Wu et al. 2017). It was reported that the maximum contents of C6 oxidized groups can vary depending on the cellulose I crystal width when the cellulose is treated with an excess amount of NaClO in the TEMPO system (Okita et al. 2010).

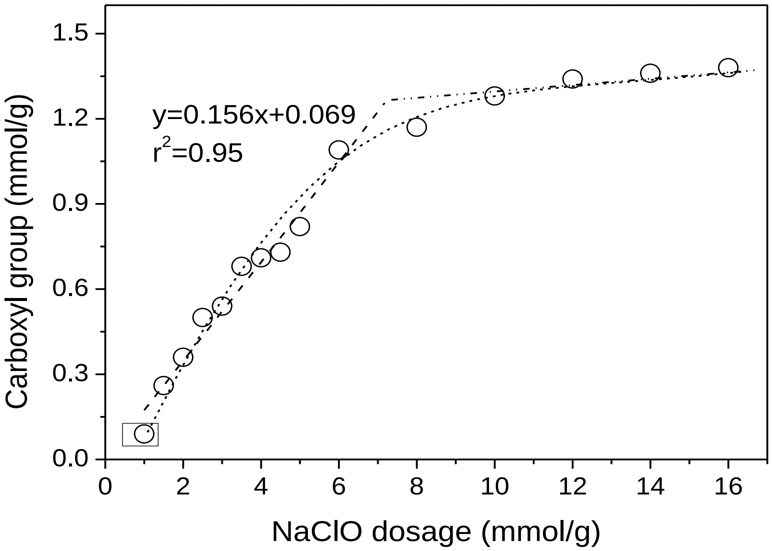

Fig. 3. The effect of NaClO dosage on the carboxyl group formation (pH 10.5, time 6 h)

The oxidation mainly occurred on the surface of the cellulose fiber, while the C6 of cellulose in the amorphous regions and the surface of crystalline are susceptible to the TEMPO/NaBr/NaClO system (Sang *et al.* 2017). The increase of the crystallinity index might account for the lingering carboxyl group formation. Figure 4 depicts the X-ray diffraction patterns of the sample and the crystallinity index. The oxidation process still kept the cellulose I of oxidized cellulose; meanwhile, the crystallinity index increased from 71.4% to 78.4% with increased NaClO addition. The crystallinity index change was almost in agreement with the change in the carboxyl group content. The results further confirmed that the oxidization resistance was attributable to the high crystallinity index and low accessibilities to the reagents (Dong *et al.* 1996; Saito *et al.* 2004).

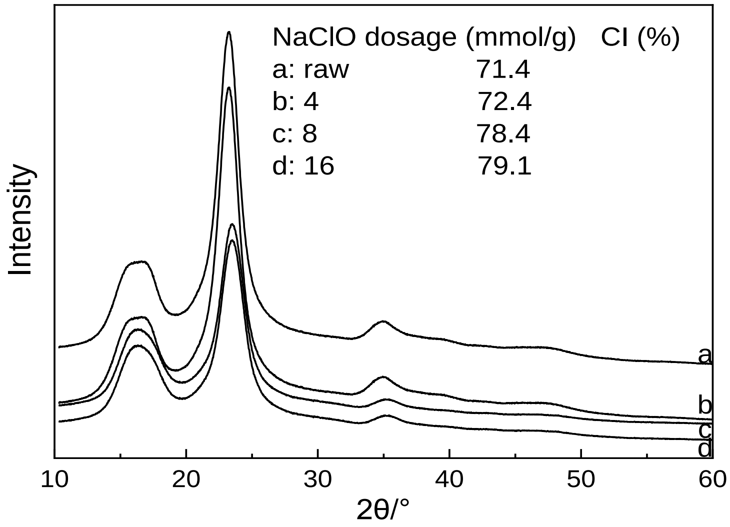

Fig. 4. XRD patterns and CI of the cellulose sample and oxidized cellulose (CI: Crystallinity index)

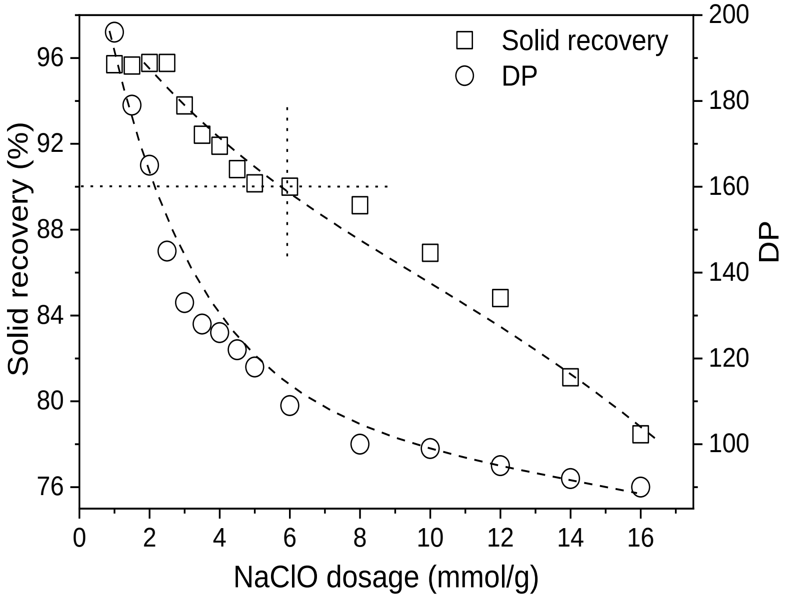

Fig. 5. The effect of NaClO dosage on the DP and solid recovery (6 h, pH 10.5)

Figure 5 depicts the effects of NaClO dosage on the DP and solid recovery. The DP and solid recovery of oxidized cellulose decreased with increasing NaClO dosage. A mild TEMPO system with only 1 mmol/g NaClO decreased the DP from 480 (starting cellulose sample) to 196. It was indicated that not only did the C6 take part in the oxidizing reaction where the primary hydroxyl was converted to carboxyl, the C1 also was involved in and initiated β-elimination and therefore cellulose cleavage (Shinoda *et al.* 2012). Furthermore, the DP evidently decreased in the case of NaClO ranging from 1 to 6 mmol/g; afterward, the DP decreased slowly. In contrast, the cellulose loss was negligible when NaClO dosage was less than 3 mmol/g; afterward, some of the oxidized cellulose was loss and showed a gradual decrease of yield.

The NaClO addition tended to optimize carboxyl groups but at the expense of cellulose degradation and even cellulose loss. Cellulose loss mainly occurred when the NaClO dosage exceeded 3 mmol/g. Fortunately the cellulose loss could be controlled beyond 10% in the case of NaClO dosage less than 6 mmol/g, where the carboxyl group increased to 1.09 mmol/g and DP was controlled at 90. To obtain oxidized cellulose with high DP and low loss, it was suggested that the NaClO dosage should be controlled at 4 to 6 mmol/g.

Effect of Reaction Time

The carboxyl content increased with increasing reaction time (Fig. 6), until a plateau was observed at 12 h or longer, while the DP and yield gradually decreased. To obtain a higher content of carboxyl groups and higher DP, the reaction time could be controlled at 4 h to 6 h. Compared to the results from Fig. 3, an extension of reaction time barely enhanced the maximum amount of carboxyl group. For example, the amount of carboxyl group was approximately 0.73 mmol/g when 6 h of reaction proceeded; with extension of time to 15 h, the maximum value was up to 0.75 mmol/g. However, with a slight increase in the dosage of NaClO, the amount of carboxyl group substantially increased. It was indicated that the amount of carboxyl group could be more dependent on NaClO dosage.

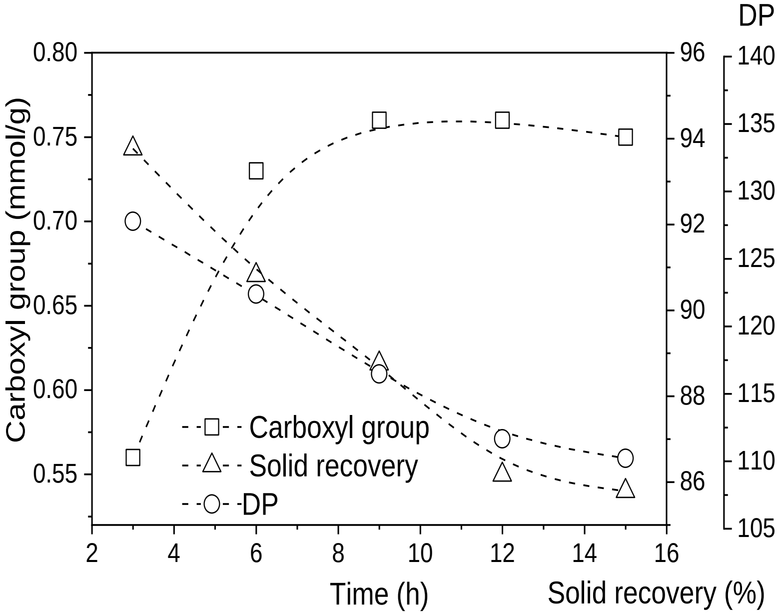

Fig. 6. Time effects (NaClO 4.5 mmol/g, pH 10.5)

CONCLUSIONS

1. The applied pH of the TEMPO/NaBr/NaClO system had a substantial influence on carboxyl group formation; the peak selective oxidation of C6 primary hydroxyls was found to occur at pH 10.5.
2. The carboxyl groups could be introduced into the wood dissolving pulp at levels up to 1 mmol/g with the cellulose loss lower than 10%. Excessive addition of NaClO could not significantly enhance carboxyl content, whereas severe cellulose degradation resulted.
3. To obtain oxidized cellulose with a relatively high carboxyl group, DP, and yield, the NaClO dosage in the TEMPO/NaBr/NaClO system should be controlled at 4 mmol/g to 6 mmol/g and the pH limited to within the range of 10 to 10.5.

ACKNOWLEDGMENTS

The authors acknowledge the support from the Canada Research Chairs Program, the National Natural Science Foundation of China (Grant Nos. 31500488 and 31770632), and the Natural Science Foundation of Fujian Province (Grant Nos. 2016J01089 and 2016H6004). The authors also acknowledge the funding support from education department of Fujian for the “Excellent talents support plan in Fujian Universities”.

REFERENCES CITED

Abe, S., Martinez-Alcala, A ., Baig, K. K. K., Saito, Y., and Monkemuller, K. (2018). “Oxidized cellulose as hemostatic agent to prevent bleeding after high-risk endoscopic resection of rectal laterally spreading tumor overlying hemorrhoids,” *Endoscopy* 50, 95-96. DOI: 10.1055/s-0043-125357

Abidi, N., Cabrales, L., and Haigler, C. H. (2014). “Changes in the cell wall and cellulose content of developing cotton fibers investigated by FTIR spectroscopy,” *Carbohydrate Polymers* 100, 9-16. DOI: 10.1016/j.carbpol.2013.01.074

Bragd, P. L., Besemer, A. C., and Van Bekkum, B. (2001). “TEMPO-derivatives as catalysts in the oxidation of primary alcohol groups in carbohydrates,” *J. Molecular Catalysis A: Chemical* 170(1-2), 35-42. DOI: 10.1016/S1381-1169(01)00061-9

Chai, X. S., Hou, Q. X., Zhu, J. Y., Chen, S. L., Wan, S. F., and Lucia, L. (2003). “Carboxyl groups in wood fibers. 1. Determination of carboxyl groups by headspace gas chromatography,” *Ind. Eng. Chem. Res.* 42(22), 5440-5444. DOI: 10.1021/ie020972a

Das, K., Ray, D., Bandyopadhyay, N. R., and Sengupta, S. (2010). “Study of the properties of microcrystalline cellulose particles from different renewable resources by XRD, FTIR, nanoindentation, TGA and SEM,” *J. Polym. Environm.* 18, 355-363. DOI 10.1007/s10924-010-0167-2

de Nooy, A. E. J., Besemer, A. C., and Van Bekkum, H. (1995). “Highly selective nitroxyl radical-mediated oxidation of primary alcohol groups in water-soluble glucans,” *Carbohyd. Res.* 269(1), 89-98. DOI: 10.1016/0008-6215(94)00343-E de Nooy, A. E. J., Besemer, A. C., Van Bekkum, H., Van Dijk, J. A. P. P., and Smit, J. A. M. (1996). “TEMPO-mediated oxidation of pullulan and influence of ionic strength and linear charge density on the dimensions of the obtained polyelectrolyte chains,” *Macromolecules* 29(20), 6541-6547. DOI: 10.1021/ma960492t

Dong, X., Kimura, T., Revol, J. F., and Gray, D. G. (1996). “Effects of ionic strength on the isotropic-chiral nematic phase transition of suspensions of cellulose crystallites,” *Langmuir* 12(8), 2076-2082. DOI: 10.1021/la950133b

French, A. D. (2014). “Idealized powder diffraction patterns for cellulose polymorphs,” *Cellulose* 21(2), 885-896. DOI: 10.1007/s10570-013-0030-4

Fukuzumi, H., Saito, T., and Isogai, A. (2013). “Influence of TEMPO-oxidized cellulose nanofibril length on film properties,” *Carbohydrate Polymers* 93(1), 172-177. DOI: 10.1016/j.carbpol.2012.04.069

Funahashi, R., Ono, Y., Tanaka, R., Yokoi, M., Daido, K., Inamochi, T., Saito, T., Horikawa, Y., and Isogai, A. (2017). “Changes in the degree of polymerization of wood celluloses during dilute acid hydrolysis and TEMPO-mediated oxidation: Formation mechanism of disordered regions along each cellulose microfibril,” *Int. J. Biol. Macromol.* 109, 914-920. DOI: 10.1016/j.ijbiomac.2017.11.078

Gamelas, J. A. F., Pedrosa, J., Lourenco, A. F., Mutjé, P., González, I., Chinga-Carrasco, G., Singh, G., and Ferreira, P. J. T. (2015). “On the morphology of cellulose nanofibrils obtained by TEMPO-mediated oxidation and mechanical treatment,” *Micron* 72, 28-33. DOI: 10.1016/j.micron.2015.02.003

Habibi, Y., Chanzy, H., and Vignon, M. R. (2006). “TEMPO-mediated surface oxidation of cellulose whiskers,” *Cellulose* 13(6), 679-687. DOI: 10.1007/s10570-006-9075-y

Hirota, M., Tamura, N., Saito, T., and Isogai, A. (2009). “Oxidation of regenerated cellulose with $NaClO_2$ catalyzed by TEMPO and NaClO under acid-neutral conditions,” *Carbohydrate Polymer* 78(2), 330-335. DOI: 10.1016/j.carbpol.2009.04.012

Isogai, A., Saito, T., and Fukuzumi, H. (2011). “TEMPO-oxidized cellulose nanofibers,” *Nanoscale* 3(1), 71-85. DOI: 10.1039/c0nr00583e

Kim, U. J., Kuga, S., Wada, M., Okano,T., and Kondo, T. (2000). “Periodate oxidation of crystalline cellulose,” *Biomacromolecules* 1, 488-492. DOI: 10.1021/bm0000337

Kuramae, R., Saito, T., and Isogai, A. (2014). “TEMPO-oxidized cellulose nanofibrils prepared from various plant holocelluloses,” *Reactive and Functional Polymers* 85, 126-133. DOI: 10.1016/j.reactfunctpolym.2014.06.011

Lal, S. S., and Mhaske, S. T. (2018). “AgBr and AgCl nanoparticle doped TEMPO-oxidized microfiber cellulose as a starting material for antimicrobial filter,” *Carbohydrate Polymer* 191, 266-279. DOI:10.1016/j.carbpol.2018.03.011

Li, J., Hu, H. C., and Chai, X. S. (2015). “Rapid method for determination of carbonyl groups in lignin compounds by headspace gas chromatography,” *Journal of Chromatography A* 1404, 39-43. DOI: 10.1016/j.chroma.2015.05.055

Ma, X. J., Cao, S. L., Lin, L., Luo, X. L., Hu, H. C., Chen, L. H., and Huang, L. L. (2013). “Hydrothermal pretreatment of bamboo and cellulose degradation,” *Bioresource Technolology* 148(7), 408-413. DOI: 10.1016/j.biortech.2013.09.021

Okita, Y., Saito, T., and Isogai, A. (2010). “Entire surface oxidation of various cellulose microfibrils by TEMPO-mediated oxidation,” *Biomacromolecules* 11(6), 1696-1700. DOI: 10.1021/bm100214b

Poletto, M., Júnior, H. L. O., and Zattera, A. J. (2014). “Native cellulose: Structure, characterization and thermal properties,” *Materials* 7(9), 6105-6119. DOI: 10.3390/ma7096105

Saito, T., and Isogai, A. (2004). “TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions,” *Biomacromolecules* 5(5), 1983-1989. DOI: 10.1021/bm0497769

Saito, T., Hirota, M., Tamura, N., Fukuzumi, H., Kimura, S., Heux, L., and Isogai, A. (2009). “Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions,” *Biomacromolecules* 10(7), 1992-1996. DOI: 10.1021/bm900414t

Saito. T., Hirota, M., Tamura, N., and Isogai, A. (2010). “Oxidation of bleached wood pulp by TEMPO/NaClO/$NaClO_2$ system: Effect of the oxidation conditions on carboxylate content and degree of polymerization,” *J. Wood Sci.* 56, 227-232. DOI: 10.1007/s10086-009-1092-7

Salminen, R., Reza, M., Pääkkönen, T., Peyre, J., and Kontturi, E. (2017). “TEMPO-mediated oxidation of microcrystalline cellulose: Limiting factors for cellulose nanocrystal yield,” *Cellulose* 24(4), 1657-1667. DOI: 10.1007/s10570-017-1228-7

Sang, X., Qin, C., Tong, Z., Kong, S., Jia, Z., Wang, G., and Liu, X. (2017). “Mechanism and kinetics studies of carboxyl group formation on the surface of cellulose fiber in a TEMPO-mediated system,” *Cellulose* 24(6), 2415-2425. DOI: 10.1007/s10570-017-1279-9

Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). “An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer,” *Textile Research Journal* 29 (10), 786-794. DOI: 10.1177/004051755902901003

Shibata, I., and Isogai, A. (2003). “Depolymerization of cellouronic acid during TEMPO-mediated oxidation,” *Cellulose* 10(2), 151-158. DOI: 10.1023/A:1024051514026

Shinoda, R., Saito, T., Okita, Y., and Isogai, A. (2012). “Relationship between length and degree of polymerization of TEMPO-oxidized cellulose nanofibrils,” *Biomacromolecules* 13(3), 842-849. DOI: 10.1021/bm2017542

Wang, M., Shao, C. Y., Zhou, S. K., Yang, J., and Xu, F. (2017). “Preparation of carbon aerogels from TEMPO-oxidized cellulose nanofibers for organic solvents absorption,” *RSC Advance* 7, 38220-38230. DOI: 10.1039/c7ra05506d

Wu, B., Geng, B., Chen, Y., Liu, H., Li, G., and Wu, Q. (2017). “Preparation and characteristics of TEMPO-oxidized cellulose nanofibrils from bamboo pulp and their oxygen-barrier application in PLA films,” *Front. Chem. Sci. Eng.* 11(4), 554-563. DOI: 10.1007/s11705-017-1673-8

Wu, C. N., and Cheng, K. C. (2017). “Strong, thermal-stable, flexible, and transparent films by self-assembled TEMPO-oxidized bacterial cellulose nanofibers,” *Cellulose* 24, 269-283. DOI: 10.1007/s10570-016-1114-8

Article submitted: March 12, 2018; Peer review completed: May 5, 2018; Revised version received: May 28, 2018; Accepted: June 1, 2018; Published: June 14, 2018.
DOI: 10.15376/biores.13.3.5965-5975