

EFFECT OF TEMPO OXIDATION SYSTEM ON KINETIC CONSTANTS OF COTTON FIBERS

Lu Dai, Hongqi Dai,* Yangchun Yuan, Xuan Sun, and Zhengjun Zhu

The kinetics of the TEMPO-mediated oxidation of cotton fibers were studied. It was revealed that the oxidation reaction of the cotton fibers by TEMPO/NaBr/NaClO system can be approximately described as two pseudo-first-order reaction kinetics that are based on the cellulose microstructure, namely the kinetic processes of the primary wall and the secondary wall. In the concentration range used in this study, the rate constant k was directly proportional to the concentration of TEMPO. As to NaBr, the rate constant was proportional to the concentration in a relatively lower range, while it tended to level off at higher concentration, but the oxidation reaction rate increased with concentration when the concentration was above 1.0 mmol/g. The pH value had a great impact on the oxidation rate; the optimum pH was controlled from 10 to 11. The effect of temperature on the rate constant could be well described by the Arrhenius equation, and the apparent activation energy measured was about 56.66kJ/mol. The X-ray diffraction pattern, which indicates the crystallinity of cotton fibers, was nearly constant during the oxidation.

Keywords: Cotton fibers; TEMPO oxidation; Kinetics; Activation energy

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INTRODUCTION

The cellulose content of the cotton cell wall is about 95%, and the crystallinity index is around 80%. It contains no lignin or surface-adsorbed lipids, and any pigments and other impurities can be easily removed. For these reasons cotton fiber is often used as a natural cellulosic fiber material to study the structure of cellulose and various chemical properties. 2,2,6,6-tetramethyl piperidine-1-oxyl radical (TEMPO), having a weak oxidizing ability, has a good selectivity to primary hydroxyl oxidation for polysaccharides (De Nooy 1994,1995a; Chang 1996). The reaction conditions are moderate, and the reaction process is relatively simple; therefore TEMPO has become a hot research topic in recent years as co-oxidant for selective oxidation of polysaccharide polymers (Isogai et al. 1998; Shibata 2003, 2005; Isogai and Yanagisawa 2008, 2009). Isogai et al. (1998) studied the TEMPO/NaClO/NaBr oxidation system on a variety of cellulose materials and for the first time used this system for a polysaccharide polymeric acid. They found out that mercerized cellulose or regenerated cellulose could be oxidized selectively. However, natural cellulose could not be completely oxidized because of its high crystallinity, and the amount of TEMPO used during the oxidation process had a great influence on the degree of polymerization of the product. Tahiri (2000) studied the

selectivity of TEMPO-mediated oxidation of amorphous cellulose and indicated that the degradation of the amorphous cellulose could be minimized.

Chemical reaction kinetics can be used to obtain a good description of the structural characteristics for the subject material. De Nooy et al. (1995b) reported a kinetic study of the TEMPO mediated oxidation of methyl α -D-glucopyranoside (MGP). Sun et al. (2005) found that in a certain concentration range the rate constant k was directly proportional to the concentration of TEMPO and to the concentration of NaBr. However, when the concentration of NaBr was above 0.4 mmol/g, the value of k no longer increased when increasing the concentration of NaBr. Fujisawa et al.'s (2010) kinetic study showed that CUA (Cellouronic acid Na salt) depolymerization rate constant roughly increased with increasing pH value or temperature. Activation energies of hydrolysis and beta-elimination of CUA were approximately 100 and 20 kJ mol⁻¹ (Fujisawa and Isogai 2010). With high crystallinity of cotton fibers, there have been no kinetic studies on the TEMPO-mediated oxidation of cotton celluloses until now. Therefore, the kinetics of TEMPO-mediated oxidation of cotton celluloses and the factors influencing the oxidation rate will be discussed in this paper.

EXPERIMENTAL

Materials

The cotton linter used in this study was a commercial pulp supplied by Snow Dragon Fiber Technology Co., Ltd., Anhui, China. TEMPO (2,2,6,6-tetramethyl piperidine-1-oxyl radical) was purchased from Johnson Matthey Co., UK. Sodium hypochlorite solution (ca. 6.0% active chlorine) was supplied by Jiuyi Chemicals Reagent (Shanghai, China). All other chemicals were analytically pure (Shanghai Chemicals Co., Ltd., China) and were used without prior purification.

Preparation of TEMPO-Oxidized Cotton Fiber

The oxidation procedure was based on the literature methodology (Saito and Isogai 2004, 2005). In brief, cotton fibers (3g) were suspended in water (225 mL) containing TEMPO (0.0075g) and sodium bromide (0.075g). Subsequently, a designed amount of NaClO solution containing 6.0% available chlorine, corresponding to 1.0 mmol/g cotton fiber, was added to the cellulose slurry under continuous stirring. The pH of the slurry was maintained at 10.5 ± 0.1 at room temperature by adding 0.05 M NaOH solution. The duration of oxidation was chosen according to the literature data (Saito and Isogai 2004), suggesting that there was no obvious increase in carboxylate content in the water-insoluble fractions during the oxidation over 4 h. After stirring for a designed time, the oxidation was quenched by adding excess ethanol. The oxidized cellulose was washed thoroughly with water, and then washed by ethanol on a filter paper set in a Büchner funnel, repeated this process about 5-6 times and dried at 40°C in a vacuum oven (Isogai and Kato 1998).

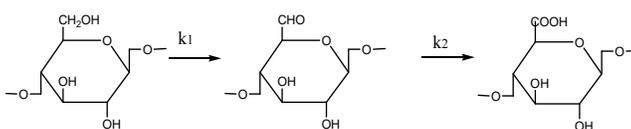
Analysis

For using in the kinetic study, the amount of carboxylic acid produced in the oxidation process was determined by a titration method. It was directly proportional to

the consumption of NaOH solution used to maintain the pH at 10.5. Sun (2005) used acid-alkaline titration and NaOH consumption per primary hydroxyl, and it was found that the carboxyl content was nearly unchanged (Sun 2005). Therefore, NaOH consumption per primary hydroxyl was used to evaluate the amount of acid produced during the process of the oxidation of the cotton fiber samples for the kinetic study.

Kinetic Study Method

The C6 hydroxyl position is selectively oxidized to an aldehyde group and then to a carboxyl form by the oxidation system. The oxidation mechanism of cotton fibers by the TEMPO/NaClO/NaBr system can be described by the following simplified scheme,



Scheme 1. Cellulose reactions in TEMPO system

where k_1 and k_2 are the rate constants of the sequential reactions. It was reported that the hydration of the aldehyde was very rapid and its oxidation was substantially more rapid than the oxidation of alcohol. Under the experimental conditions used in this study, we assumed that the oxidation reaction of the cotton fibers can be dealt with in a consecutive first-order reaction system with $k_2 > k_1$ (Sun 2005).

For a first-order reaction, the reactants $A \rightarrow$ products, the differential rate equation can be given as:

$$-dC_A/dt = k_A C_A \quad (1)$$

This relationship also allows separation of variables, as follows:

$$-dC_A/C_A = k_A dt \quad (2)$$

For the reaction time from $0 \rightarrow t$, the corresponding concentration of component A can be described by the term $C_{A,0} \rightarrow C_A$,

$$-\int_{C_{A,0}}^{C_A} \frac{dc_A}{c_A} = \int_0^t k_A dt \quad (3)$$

where K_A is a rate constant. The integration of Eq. (3) yields

$$\ln(c_{A,0}/c_A) = k_A t \quad (4)$$

The conversion can be expressed as,

$$\ln c_A = -k_A t + \ln c_{A,0} \quad (5)$$

or alternatively in the following form:

$$c_A = c_{A,0} \exp(-k_A t) \quad (6)$$

Thus, the TEMPO/NaClO/NaBr oxidation system for cotton fiber oxidation rate equation can be expressed as follows:

$$[\text{CELL}-\text{CH}_2\text{OH}]_t = [\text{CELL}-\text{CH}_2\text{OH}]_0 \exp(-k_1 t) \quad (7)$$

$$[\text{CELL}-\text{CHO}]_t = [\text{CELL}-\text{CH}_2\text{OH}]_0 \left\{ \frac{k_1}{k_2 - k_1} \right\} \left\{ \exp(-k_1 t) - \exp(-k_2 t) \right\} \quad (8)$$

Equations 7 and 8 can be further simplified with an approximation,

$$\begin{aligned} [\text{CELL}-\text{COOH}]_t &= [\text{CELL}-\text{CH}_2\text{OH}]_0 \{1 - \exp(-k_1 t)\} \\ \ln([\text{CELL}-\text{CH}_2\text{OH}]_0 - [\text{CELL}-\text{COOH}]_t) &= -k_1 t + \ln[\text{CELL}-\text{CH}_2\text{OH}]_0 \end{aligned} \quad (9)$$

where $[\text{CELL}-\text{CH}_2\text{OH}]_0$ and $[\text{CELL}-\text{COOH}]_t$ represent the amount of C6 hydroxyl group present in the celluloses and the carboxyl group at time t . The concentration $[\text{CELL}-\text{COOH}]_t$ can be indirectly determined by the concentration of sodium hydroxide. From the slope of the plots of $\ln([\text{CELL}-\text{CH}_2\text{OH}]_0 - [\text{CELL}-\text{COOH}]_t)$ versus t , the rate constant k can be determined. For simplicity and uniformity, this paper will set $C([\text{CELL}-\text{CH}_2\text{OH}]_0 - [\text{CELL}-\text{COOH}]_t)$ to C_A , as the concentration of reactants after the time t .

X-ray Diffraction

The dried cotton fiber samples were converted to powder substrates, and subjected to X-ray diffraction analysis from 5° to 40° at $5^\circ/\text{min}$ of diffraction angle 2θ using the reflection method by means of a D/Max-3A (Japan) with a Nifiltered $\text{CuK}\alpha$ radiation ($\lambda = 0.1548\text{nm}$) at 40 kV and 100 mA. The crystallinity indices based on 2θ scan from 5° to 40° were calculated according to the Segal's method,

$$\text{Crystallinity} = (I_{002} - I_{AM}) \times 100\% / I_{002} \quad (10)$$

where I_{002} was identified with the intensity at 22.5° , and I_{AM} was the intensity at 18.6° .

RESULTS AND DISCUSSION

Kinetic Analysis

Through a series of studies in this experiment, it was found that specific carboxyl contents of cellulose fiber preparation conditions could be obtained by changing the oxidation time, oxidation temperature, pH value, and oxidant (NaClO) dosage. In the oxidation process, the reaction ratio increased with the increased amount of TEMPO and NaBr. However, the carboxyl content of cotton fiber became a constant during the final oxidation stage. This indicated that in the oxidation system, TEMPO and NaBr only acted as catalysts; they could not increase the carboxyl content. Typical curves for the

oxidation of cotton fiber are shown in Fig. 1. For more intuitive representation of the reaction process, the time was extended to 8 hours.

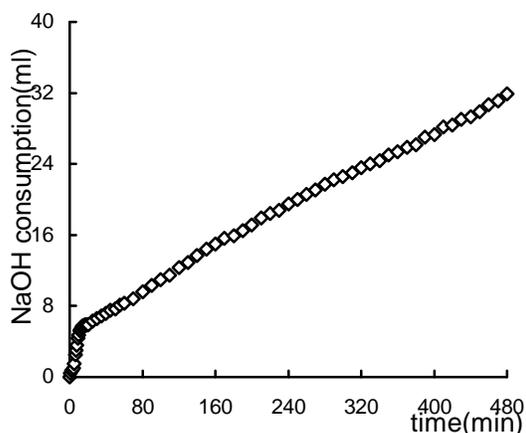


Fig. 1. The oxidation of cotton fiber as measured with pH-stat

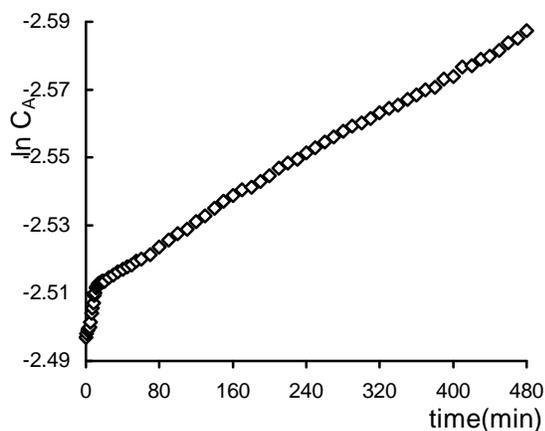


Fig. 2. Plots of $\ln C_A$ versus time for the oxidation of cotton fiber

It could be seen that oxidation of cotton fiber was more rapid at the beginning, which was possibly due to the microstructure of fiber. In the initial stage, the reaction proceeded easily, and the reaction rate was high because of the loose, random structure of microfibrils in the primary wall area. When the reaction time exceeded 15 minutes of oxidation, there was a decrease of the reaction rate, which was attributed to the end of the reaction in the primary wall area of cotton fibers and then the start in the secondary wall area. But each layer of microfibrils formed the layer membrane structure in some approximately parallel way, and the arrangement angle of the microfibrils was different, impeding further reaction as the result of the diffusion phenomenon. Research reported in a patent (Thomaides 2003a,b) showed that in the process of TEMPO oxidation of the C6 primary hydroxyl to carboxyl, a large number of aldehyde groups would be produced in the initial period between 5 and 15 minutes. The aldehyde groups quickly became carboxyl groups as time passed. De Nooy et al. (1995b) have reported a kinetic study of the TEMPO-mediated oxidation of methyl α -D-glucopyranoside (MGP), in which an induction period appeared to be due to the formation of an aldehyde intermediate and a build-up of the nitrosonium ion.

Based on the information in Fig. 1 (process data), when evaluated according to a characteristic of first-order reaction, $\ln C_A$ was plotted as a function of time for the oxidation of cotton fiber (Fig. 2). It is clear that a straight line could be fit over a wide range of time, indicating that the formation of carboxylic acid was first-order with respect to the substrate. However, in the oxidation time interval from 0 to 15 minutes, a rapid rate of oxidation reaction in this period could be seen, and then the reaction gradually slowed down, so the oxidation of cotton fiber could be divided into two sections of dynamic equation intervals: the early period corresponded to the oxidation reaction in primary wall of the fiber, and the second period involved only the more gradual oxidation reaction of the secondary wall. According to the figures above and the special structure

of cellulose, the dynamic process could be split as shown in Figs. 3 and 4, according to the two reaction periods.

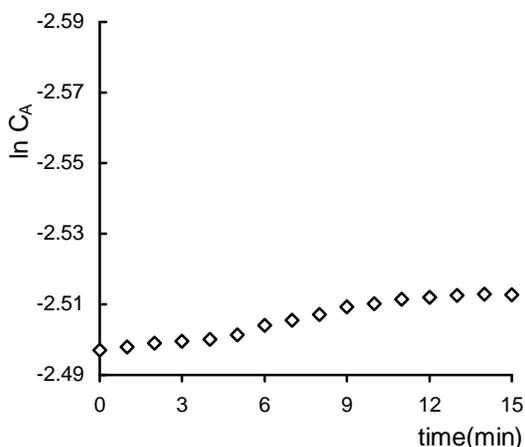


Fig. 3. Plots of $\ln C_A$ versus time for the primary wall area

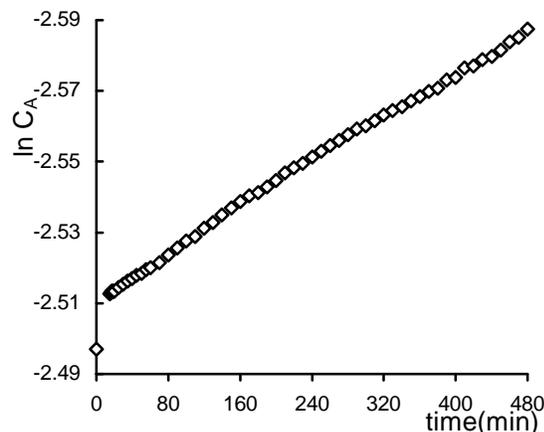


Fig. 4. Plots of $\ln C_A$ versus time for the secondary wall area

From Figs. 3 and 4 it is apparent that the two curves were very consistent with the requirements of the first-order reaction kinetics. In the primary wall area, based on the linear regression equation for this stage, the rate k_1 was $1.2 \times 10^{-3} \text{ min}^{-1}$. When the reaction took place deeply in the secondary wall area (after the primary wall area had been removed), the reaction rate k_2 was $0.2 \times 10^{-3} \text{ min}^{-1}$, only one-sixth of that in primary wall area. This difference could be due to the accessibility of the primary wall and secondary wall areas for oxidant in the microstructure of cotton fibers, for which the oxidation reaction could take place more easily in the primary wall area than that of secondary wall area.

Influence of the TEMPO Concentration on the Rate of Oxidation of Cotton Fiber

Figure 5 shows the curve of NaOH consumption rate plotted as function of time for different TEMPO concentrations. From the figure it can be seen the oxidation rate was gradually increased with increasing the amount of TEMPO catalyst. But with the gradual oxidation of the fiber, the primary wall area became completely reacted, and the reaction of secondary wall fibers continued farther, so that the reaction rate became flat. As the figure shows, the oxidation of the primary wall area needed around 20 min when the amount of the TEMPO was 0.008 mmol/g, and when the dosage increased to 0.032 mmol/g, the oxidation time of the primary wall area required 10 min. With respect to the reaction in the secondary wall area, the reaction rate was almost free from the influence of the catalyst, and the final carboxyl content was almost the same, independent from TEMPO concentration. The amount of catalyst only increased the reaction rate. By processing the data from Fig. 2 and constructing a diagram of $\ln C_A$ vs. t , it was clear that the curves were very consistent with the requirements of first-order reaction kinetics. By the linear regression for TEMPO usage levels from 0.008 mmol/g to 0.032 mmol/g (dry pulp) for the primary wall area, the reaction rate constants were $2.7 \times 10^{-3} \text{ min}^{-1}$, 3.4×10^{-3}

min^{-1} , $3.7 \times 10^{-3} \text{ min}^{-1}$, and $4.3 \times 10^{-3} \text{ min}^{-1}$. The secondary wall area reaction rate constant was $0.2 \times 10^{-3} \text{ min}^{-1}$ at each TEMPO dosage. Thus, the oxidation rate increased with the amount of TEMPO.

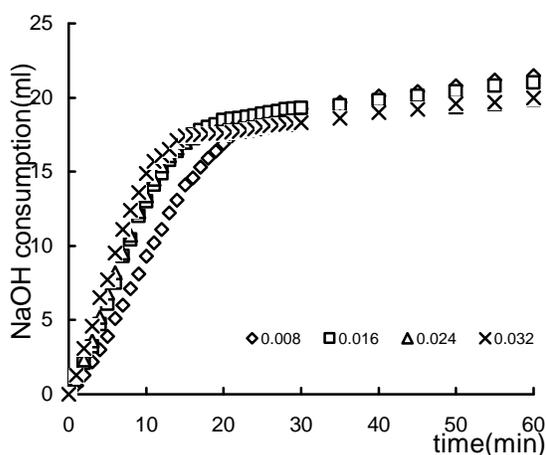


Fig. 5. Plots of TEMPO concentration vs. NaOH consumption for the oxidation of cotton fiber

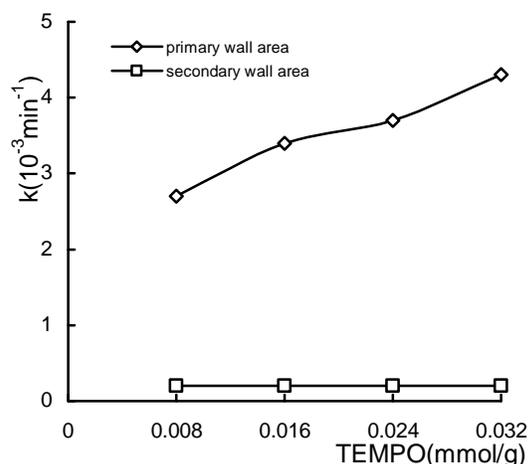


Fig. 6. Influence of the TEMPO concentration on the rate of oxidation of cotton fiber

In order to more intuitively demonstrate the amount of catalyst and oxidation rate constant, the oxidation rate constant k was plotted as a function of TEMPO concentration. It could be seen from Fig. 6 that a linear relationship existed between the rate constant k and the TEMPO concentration, which indicated that at a certain concentration range, the oxidation reaction rate was proportional to the concentration of TEMPO. De Nooy et al (1995b) found that the oxidation reaction rate of their MGP sample depended on the concentrations of MGP, TEMPO, and NaBr in the TEMPO/NaClO/NaBr system.

Influence of NaBr Concentration on the Rate of Oxidation of Cotton Fiber

Figure 7 shows the NaOH consumption rate as a function of NaBr concentration. The plotted curves represent different molar concentrations of NaBr. From the figure it can be seen that the oxidation rate gradually increased and then decreased with increasing NaBr catalyst. However, with the oxidation of the fiber, the primary wall area became depleted, and the reaction rate in the deep secondary wall area became marginal, as indicated by the rate of consumption of TEMPO. The oxidation of the primary wall area required around 15 min when the amount of the NaBr was 0.25 mmol/g, and when the dosage was increased to 1.0 mmol/g, the oxidation needed only 6 minutes. By contrast, for the reaction in the secondary wall area, the reaction rate was almost free from the influence of the catalyst, and the final extent of reaction of the carboxyl content were almost the same. An increased amount of catalyst only increased the reaction rate, not the ultimate extent of reaction. By processing the data from Fig. 2 and constructing a $\ln C_A$ vs. t diagram, it was clear that the curves were consistent with the requirements of first-order reaction kinetics. Based on the linear regression, NaBr usage from 0.25 mmol/g to 2.0 mmol/g (dry pulp), the reaction rate constants were $3.4 \times 10^{-3} \text{ min}^{-1}$, $3.8 \times 10^{-3} \text{ min}^{-1}$, $6.2 \times 10^{-3} \text{ min}^{-1}$, and $4.8 \times 10^{-3} \text{ min}^{-1}$.

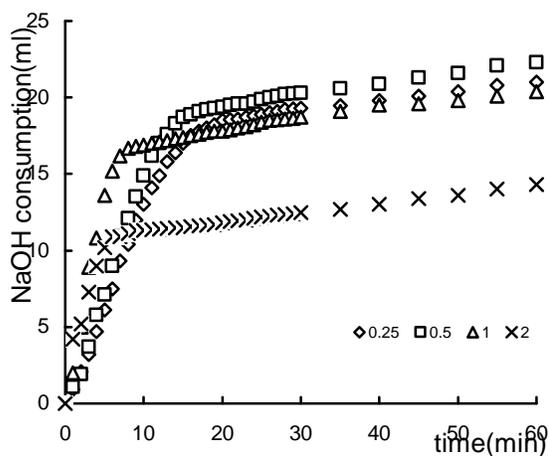


Fig. 7. Plots of NaBr concentration versus NaOH consumption for the oxidation of cotton fiber

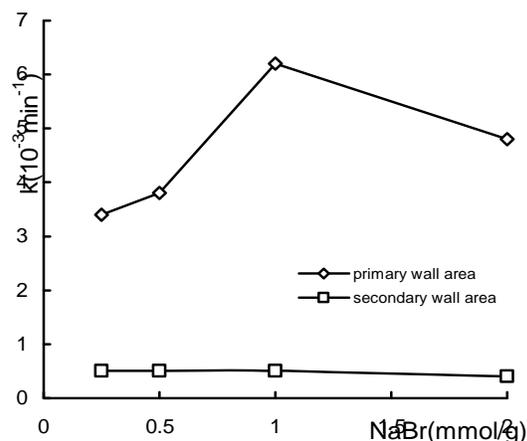


Fig. 8. Influence of the NaBr concentration on the rate of oxidation of cotton fiber

For the secondary wall area the corresponding reaction rate constants were $0.5 \times 10^{-3} \text{ min}^{-1}$, $0.5 \times 10^{-3} \text{ min}^{-1}$, $0.5 \times 10^{-3} \text{ min}^{-1}$, and $0.4 \times 10^{-3} \text{ min}^{-1}$. In order to more intuitively demonstrate the effects of the amount of catalyst and oxidation catalyst, the oxidation rate constant k was plotted as function of NaBr concentration. It could be seen from Fig. 8 that a linear relationship existed between the rate constant k and the NaBr concentration within the range 0.25 to 1.0 mmol/g, but the oxidation reaction rate decreased with concentration when the concentration was above 1.0 to 2.0 mmol/g. This might be explained based on a hypothesis that the excess of NaBr concentration suppressed the formation of HOBr oxidant, causing the reaction rate to be diminished.

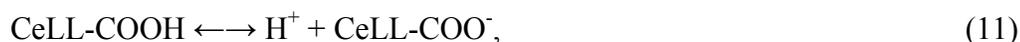
Influence of the pH Value on the Rate of Oxidation of Cotton Fiber

Table 1 presents the kinetic data measured for the oxidation of cotton fiber as it was affected by pH. In general it was advantageous to the reaction process to increase the pH, but the oxidation rate decreased if the pH of the system was above 11. The results suggested that the system pH could be controlled to an optimum level, since side reactions between excess NaOH and fibers apparently led to the degradation of the fibers.

Table 1. Kinetic Data Measured for the Oxidation Reaction at Various pH Values

Reaction Condition	pH	Temperature °C	TEMPO mmol/g	NaBr mmol/g	NaOCl mmol/g	k 10^{-3} min^{-1}
1	8.5	25	0.016	0.25	1.0	2.4
2	9.0	25	0.016	0.25	1.0	2.5
3	9.5	25	0.016	0.25	1.0	3.0
4	10.0	25	0.016	0.25	1.0	3.1
5	10.5	25	0.016	0.25	1.0	3.4
6	11.0	25	0.016	0.25	1.0	3.6
7	11.5	25	0.016	0.25	1.0	3.2

Comparing the rate constants corresponding to different pH values of the solutions in Table 1, the influence of the reaction pH on the rate of oxidation was also obvious. The oxidation rate increased with increasing pH within the range from 8.5 to 11. Dang (2007) discovered that hypochlorous acid turned into a nonselective oxidant with very strong, but uncontrolled oxidizing ability, and at the same time, reactivity of TEMPO decreased and the reaction rate decreased. De Nooy (1995a), in a study of water-soluble polysaccharides and their ramifications, discovered that the reaction rate constant was reduced as pH was increased beyond 11. The phenomenon of our experiment was the same as theirs. In addition, the exterior carboxyl content of the cotton fibers increased with increased pH, according to the conclusions of the experiment. However, exterior carboxyl content decreased when the pH exceeded 11. On the one hand, this could be attributed to the fact that supplementary NaOH raised the pH sufficiently to cause a hysteresis effect, which increased the oxidation degree of fiber, causing significant degradation. On the other hand, the carboxyl is ionized under alkaline conditions. The carboxyl is a weakly acidic group, and it ionizes partly in water. Its ionization formula is



and its ionization equilibrium constant is given by

$$K_a = \frac{[\text{H}^+][\text{CeLL-COO}^-]}{[\text{CeLL-COOH}]}. \quad (12)$$

The ionization equilibrium of carboxyl is influenced by the pH of the system. The reaction is shifted towards right by increasing pH, *viz.*, by reducing the H^+ concentration. With increasing content of CeLL-COO^- , the negative charge of the fibers became stronger. However, Shibata et al. (2006) proved that it was possible to form a hydroxyl radical from the hydroxylamine and NaBrO followed by β elimination, and that such a mechanism participated in depolymerization under alkaline conditions, which led to the obvious decrease of the fiber molecular weight. Although the electronegativity of the fiber exterior became strong and the degree of ionization decreased, the carboxyl content decreased with pronounced degradation (Shibata and Isogai 2003; Hirota and Tamura 2009). Besides, in alkaline conditions, the hydroxyl groups of the fiber exterior partly became negative that increased with the increase in pH. Sodium hypochlorite dissociated into ClO^- , which carries a negative charge, so that a repulsive interaction affected the oxidation. Consequently, increasing the pH limited the rate of oxidation. As a result, in reference to the oxidation rate, the optimum pH was controlled from 10 to 11 during the TEMPO/NaClO/NaBr oxidation.

Rate Constants and Activation Energy of Oxidation of Cotton Fiber

The effect of catalyst concentration on the oxidation rate of cotton fiber has been early discussed. The experimental results have made it obvious that temperature is also an important factor. It can be seen from the formula that $d(\ln k)/dT$ increases along with E_a , so with high activation energy, it is more obvious that the reaction rate increase with elevated temperatures. In other word, increased temperature is beneficial to reactions

under the situation with high activation energy. Figure 9 shows the curves of NaOH consumption rate plotted as function of time at different temperatures.

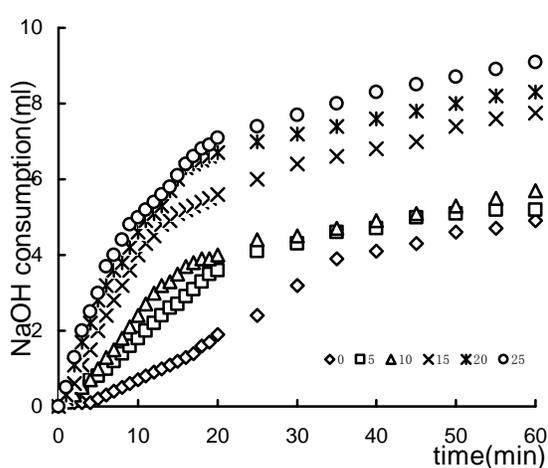


Fig. 9. Plot of temperature versus NaOH consumption for the oxidation of cotton fiber

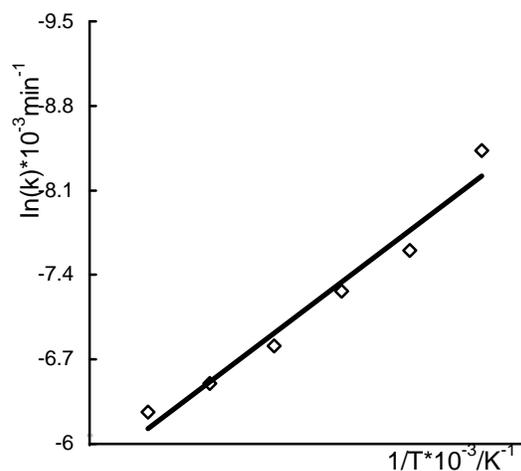


Fig. 10. Arrhenius Plot for the oxidation of cotton fiber in the range of 0°C to 25°C

From Fig. 9, the effect of temperature on the oxidation reaction rate can be clearly seen. The reaction rate was low and almost in a linear relationship when the temperature was about 0°C. The speed of the NaOH consumption almost formed a linear relationship with time. The slope of the curve was increased along with the increasing temperatures, which indicated that the oxidation rates will increase and that the process needs less time for oxidation of the primary wall area. Constructing a diagram of $\ln C_A$ vs. t with data from Fig. 2, it was obvious that the curves fit well to first-order reaction kinetics. With the different temperature levels from 0°C to 25°C, the reaction rate constants were $0.2 \times 10^{-3} \text{ min}^{-1}$, $0.5 \times 10^{-3} \text{ min}^{-1}$, $0.7 \times 10^{-3} \text{ min}^{-1}$, $1.1 \times 10^{-3} \text{ min}^{-1}$, $1.5 \times 10^{-3} \text{ min}^{-1}$, and $1.8 \times 10^{-3} \text{ min}^{-1}$. Thus, the oxidation rate will increase with increasing temperature. In 25°C, the reaction rate constant increased by a factor of 9 compared with reaction in 0°C.

A good linear relationship between the different temperature and the reaction rate constant could be seen from Fig. 10. The line slope was 6.814 after a linear regression, from which the apparent activation energy calculated is 56.66 kJ/mol.

Crystallinity of Cotton Fiber during TEMPO-Mediated Oxidation

Figure 11 shows X-ray diffraction patterns of the cotton fibers before and after the TEMPO-mediated oxidation. From Fig. 11 and the experimental data of crystallinity degree it may be concluded that although the yield of cotton fibers was decreased by oxidation, the X-ray diffraction patterns were barely changed even after the oxidation, indicating that the fiber retained its crystal morphology. The 2θ diffraction angle of cotton fiber was changed slightly through the oxidation; these slight changes might be caused by the introduction of significant amount of carboxyl and aldehyde groups on the crystal surfaces. Generally the oxidation did not reach to the interior of the crystalline region, in agreement with earlier findings (Saito and Isogai 2004).

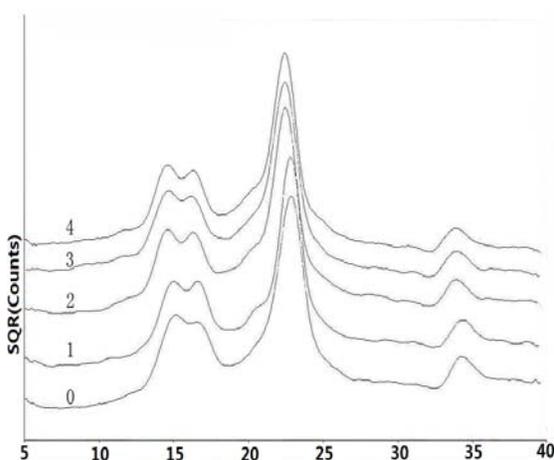


Fig. 11. X-ray diffraction patterns of the original (0) and after the TEMPO-mediated oxidation at times of 0.25h (1), 0.5h(2), 4h(3), 12h(4) at room temperature

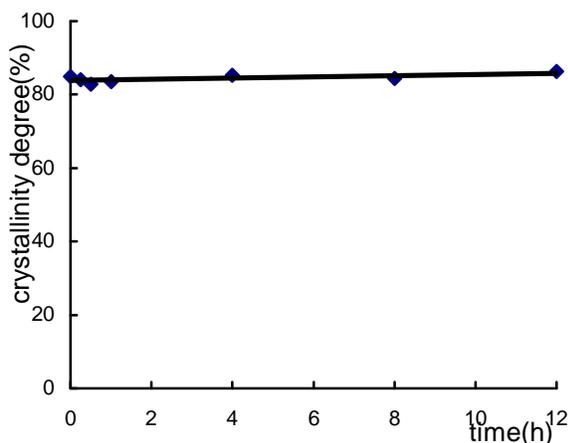


Fig. 12. Plots of pretreatment time versus crystallinity degree for the oxidation of cotton fiber

Figure 12 shows that there was little influence of different pretreatment times on crystallinity degree. From the figure it can be concluded that neither carboxyl nor aldehyde groups were formed inside crystallites during the TEMPO-mediated oxidation; the significant amounts of carboxyl and aldehyde groups formed in the water-insoluble fractions were mostly present on the crystal surfaces and in amorphous regions. Thus, the TEMPO-mediated oxidation of cellulose cotton fiber could introduce carboxyl and aldehyde groups with high densities in amorphous regions and on crystal surfaces, maintaining the water-insoluble nature of the material.

CONCLUSIONS

1. The oxidation of the cotton fibers can be approximately described in terms of two pseudo-first-order reaction rates based on the cellulose microstructure, namely the kinetic process of the primary wall area and that of the secondary wall area.
2. The rate constant k was directly proportional to the concentration of TEMPO usage from 0.008 mmol/g to 0.032 mmol/g and NaBr usage from 0.25 to 1.0 mmol/g, though it decreased when the concentration of NaBr was above 1.0 mmol/g. The pH value had a great impact on oxidation rate; the optimum pH was controlled from 10 to 11. The apparent activation energy was about 56.66 kJ/mol according to the measurement.
3. The X-ray diffraction pattern indicated that crystallinity of cotton fibers remained nearly constant during the oxidation.

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