Influencing Factors for Alkaline Degradation of Cellulose

Qun Li,[a,]* Aijiao Wang,[a] Wenhui Ding,[b] and Yujia Zhang [c]

Different factors that influence the alkaline degradation of cellulose in the pulping process were considered in this study. The factors were the reaction temperature, reaction time, dosage of NaOH, and metal ions. Microcrystal cellulose (MCC) was applied as the model compound. To measure the influence of different metal ions on the alkaline degradation of cellulose, K^+ and Mg^{2+} were added into the reaction system. The Fourier transform infrared (FTIR) spectra of the MCC in the solution with and without K^+ and Mg^{2+} were analyzed to clarify the reaction mechanism of the alkaline degradation of cellulose and MCC. Alkaline degradation increased with increasing reaction temperature, reaction time, and alkali concentration. When the reaction temperature was above 80 °C, the reaction time was above 2 h, or the alkali content was below 5 g/L, the degradation ratio of MCC decreased. The amount of degraded MCC and the concentration of glucose in the reaction solution exhibited a nearly linear relationship when the alkali quantity increased from 0 g/L to 5 g/L. K^+ and Mg^{2+} had an opposite impact on the alkaline degradation. While the K^+ promoted the alkaline degradation of cellulose, the Mg^{2+} inhibited it, along with an increase of the dosage of the two metal ions.

Keywords: Alkaline degradation; MCC; Metal ions; FTIR

*Contact information: a: Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, China; b: Xianning City Environmental Protection Agency, Hubei Province, China; c: School of Chemical Science and Engineering, Royal Institute of Technology, Stockholm, Sweden; * Corresponding author: liqun@tust.edu.cn*

INTRODUCTION

Cellulose is the building block of all plant life; it constitutes a significant portion of the plant biomass (Zaman *et al*. 2012) and is widely used in the pulp and paper industry. It is a linear polymer of D-glucose residues that is linked by β-1 and 4-glycoside bonds (Kobayashi *et al*. 2011; Yoon *et al*. 2008). Each cellulose unit contains three hydroxyl-groups, which, together with lignin and hemicellulose, form complex spatial networks of inter- and intra-molecular hydrogen bonds (Northolt *et al*. 2001; Butera *et al*. 2011). This network not only prevents cellulose from being degraded, but is also one of the reasons for its indissolubility in the solvents. However, alkaline degradation or thermal degradation always occurs during the pulp and paper process, resulting in a decrease in the cellulose and hemicelluloses content in the pulp or paper.

The alkaline degradation of cellulose is a well-known phenomenon in the pulping and textile industries (Pavasars *et al*. 2003). It has also been studied in relation to the transformation of biomass to various low-molecular-weight products (Das Gupta and Day 1984). Unfortunately, the cellulose and hemicelluloses are partly degraded and dissolved in an alkaline solution, which is undesirable due to the decrease of yield and molecular weight of cellulose and hemicelluloses (Berggren *et al*. 2003).

The rate of cellulose degradation depends on the form of the cellulose (Helmy 1993; Askarieh *et al*. 2000). In nearly all modes of cellulose degradation, the cellulose supra-molecular structure, such as crystallinity or fibrillar morphology, plays a decisive role in determining the rate and the course of cellulose degradation. A high supra-molecular order of the polymer chain generally impedes degradation (Klemm *et al*. 1998). Amorphous cellulose reacts more readily than crystalline cellulose (Greenfield *et al*. 1994). Therefore, the alkaline degradation is more rapid in the amorphous regions compared with the crystalline regions.

Microcrystalline cellulose (MCC) is obtained at an industrial scale through the hydrolysis of wood and cotton cellulose using dilute mineral acids (Suzuki and Nakagami 1999; El-Sakhawy and Hassan 2007). It is a purified partially depolymerised non-fibrous form of cellulose, which occurs as a white, odourless, tasteless, crystalline powder composed of 20 to 80 μm porous particles. The crystal structure of MCC is that of cellulose I, and the ultimate degree of polymerization in the range 15 to 375 (He *et al.* 2010; Eichhorn *et al.* 2001).

The MCC particles ranged in size from 20 µm to 80 µm. In this experiment, MCC was elected as the model to explain the effect of metal ions on the alkaline degradation of cellulose under low temperature and alkaline condition, because it reserves the crystallinity of cellulose I, and its crystallinity and crystal size are higher than original cellulose.

When cellulosic fibers are subjected to thermal degradation, a series of physical and chemical changes occur. The affected physical and chemical properties include enthalpy, color, and the orientation of cellulose with viscosity and molecular weight with DP. The major change of cellulosic fibers in thermal degradation is to enhance the reactivity of the crystalline cellulose through decreasing the DP and increasing the accessibility of cellulose (Liu *et al*. 2012). The thermal degradation of cellulose occurs through a series of complex mechanisms that are difficult to evaluate (Kim *et al*. 2010).

In this study, the alkaline degradation of cellulose was examined. Natural cellulose was divided into an amorphous region and a crystallization region. An intra-molecular hydrogen bond and an intermolecular hydrogen bond, as well as the complexity of the state of aggregation in the crystallization region, cause a negative effect on the solubility and reaction performance. This effect influenced the reactivity of cellulose in the crystallized region, but the reactivity of cellulose in the amorphous region was very good. The amorphous area almost was non-existent in the structure of the MCC. MCC with high purity was used as the model compound to investigate how the alkaline degradation of cellulose was affected by the different factors, especially the cellulose in the crystallization region.

EXPERIMENTAL

Materials

Analytical grade NaOH, KCl, and $MgCl_2 \cdot 6H_2O$ were used for the control of the alkali charge and the metal ions in this experiment. MCC (Kelong Chemical Reagent, Beijing, China), which was biochemical reagent level, was chosen as the reactant. 3, 5-Dinitro-salicylic acid (DNS) was used to determinate the content of the glucose in the reaction solution with a UV-1600 visible spectrophotometer (Ruili Analytical Instrument Co., Ltd, Beijing, China) (Saqib and Whitney 2011).

Methods

Along with changing reaction conditions, the degree of alkaline degradation was varied. The degradation of cellulose generated reducing sugar, which was quantified to indicate the degree of alkaline degradation.

Reaction conditions

The reaction conditions that could influence the alkaline degradation of cellulose were the reaction temperature, reaction time, dosage of alkali, and the concentrations of different metal ions. The range of temperature and reaction time was 60 °C to 90 °C and 1 h to 4 h, respectively; 0 g/L to 7.5 g/L of NaOH and the same range of 0 g/L, 0.75 g/L, 1.5 g/L, and 2.25 g/L of Mg^{2+} and K^{+} were added into the solution to explore the effects of metal ions on the alkaline degradation. The experiment was completed in a closed stainless steel reactor, which is isolated from the air to eliminate the effects of CO_2 as far as possible.

After 0.5 g of MCC was added into 20 mL of deionized water, the NaOH and metal ions were added to control the degradation degree of MCC. Lastly, the MCC residue was subsequently washed with deionized water until it was neutralized.

Quality determination of MCC residue

The degree of alkaline degradation was expressed as the weight ratio of the remained MCC *versus* the added MCC. Before being used, the MCC was dried to a constant weight at 105 °C ± 2 °C, the mass of the needed MCC was 0.5 g. After the reaction, the MCC remnants were obtained through filtration with drying at 105 °C and were then weighed.

Reducing sugars measurement assay

The peeling reaction can remove only one glucose unit at a time from the reducing end, while the hydrolysis reaction can cause the breaking of cellulose chains. Since the porosity and much lower DP of MCC (the cellulose in plant fiber generally more than 10000), the MCC is actually much more reactive than the crystalline zone in the fiber, and the effect of hydrolysis reaction can be more significant than peeling reaction. In this work the DNS method was used for the determination of the content of reducing sugar, representing the MCC degradation products.

The 3,5-dinitrosalicylic acid (DNS) colorimetric method is based on the simultaneous oxidation of functional sugar groups and the reduction of DNS to 3-amino-5-nitrosalicylic acid upon the application of alkaline conditions and heat. This method has been extensively used to measure sugars with a reducing property that are generated by the presence of a potential aldehyde- or keto-group (Teixeira *et al*. 2012).

Glucose was used at a concentration range of 0 mL to 14 mL (the concentration was 1 mg/mL) in order to draw the best standard curve. The linear regression equation was $y = 1.6137\ x + 0.1091$, where, x represents the concentration of the glucose standard solution and y represents the absorbance. The coefficient of linear correlation was 0.9996, which showed the relationship between the concentration of the glucose standard solution and absorbance.

Because of their usefulness and ease of use, the DNS reagent composition and assay conditions were further optimized for each compound concentration, boiling time, and dilution ratios. The reaction mixtures contained 2 mL of the relevant reducing sugar solution and 1.5 mL of either DNS reagent. The reaction mixture was boiled in a water bath for 15 min and cooled to room temperature in a water-ice bath. Subsequently, the solution was diluted to 25 mL with distilled water and made to stand for 30 min. The absorbance was measured at 510 nm using a UV-1600 spectrophotometer.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was used to analyze structural changes in the MCC residue. The KBr compression method was applied to record in room temperature (22 °C). The mixing ratio of the samples with the KBr, the scan wavelength range, and scan times were 1:300, 500 cm^{-1} to 4000 cm^{-1}, and 32, respectively.

RESULTS AND DISCUSSION

Effect of the Reaction Temperature on the Alkaline Degradation of MCC

Figure 1 shows the effect of the reaction temperature on the amount of MCC residue and the concentration of glucose in the reaction solution. With increasing reaction temperature, the amount of MCC residue decreased considerably, while the concentration of glucose increased dramatically. In other words, the degree of degradation increased with increasing temperature. Furthermore, the weight loss of MCC reached about 35%, demonstrating that the crystal region of cellulose was degraded under the alkali reaction and oxidation at 80 °C, although the mechanism is still unclear.

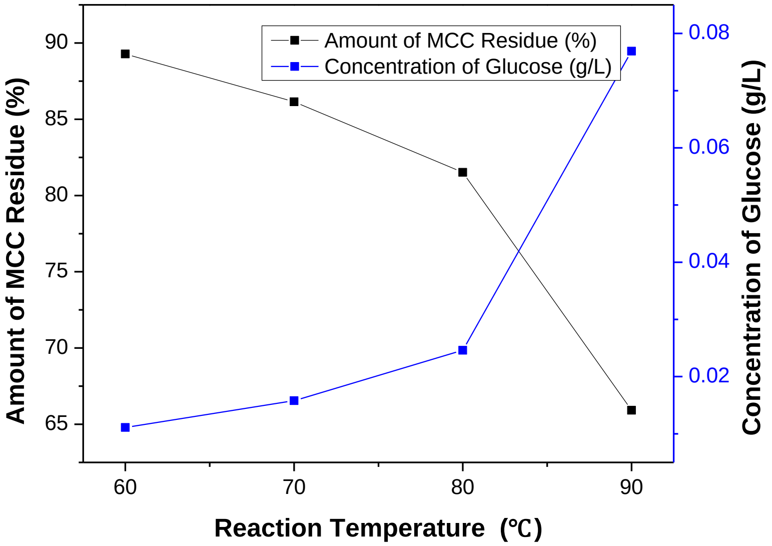

Fig. 1. The amount of MCC residue and the concentration of glucose in the reaction solution as functions of the different reaction temperature. The concentration of NaOH was 5 g/L, and the reaction time was 4 h.

Effect of the Reaction Time on the Alkaline Degradation of MCC

As shown in Fig. 2, the degradation of MCC and the concentration of glucose increased with prolonged reaction time. Within the initial 2 h, the alkaline degradation of MCC was vigorous but slowed down after 2 h, and the trend of the glucose content in the reaction solution was similar to that of the degraded MCC. In the initial period of reaction, the termination reaction made reducing end groups reacting with alkali easily translate into α- or β-partial sugar acid groups, which can prevent the decline of reducing glucose, but the termination reaction had not yet occurred. The amount of degraded MCC and the concentration of glucose increased sharply at first. The degradation became slower for the termination reaction to occur, which stabilized the structure of the cellulose and slowed the rate of alkaline degradation.

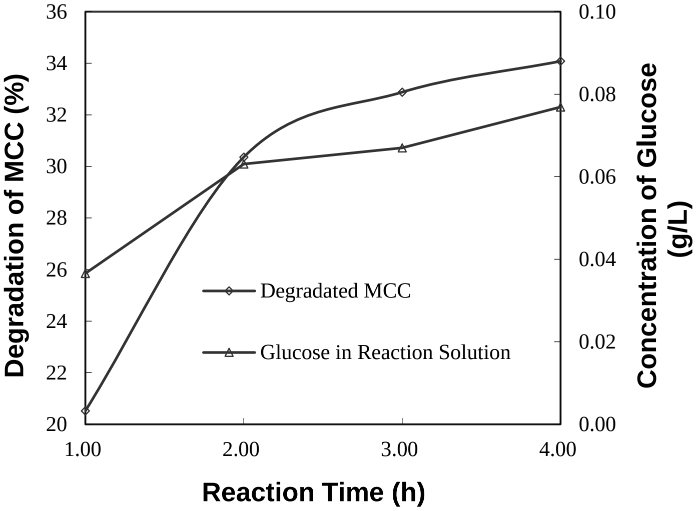

Fig. 2. Degradation of MCC and the concentration of glucose in the reaction solution as functions of the different reaction time. The concentration of NaOH was 5 g/L, and the reaction temperature was 90 °C.

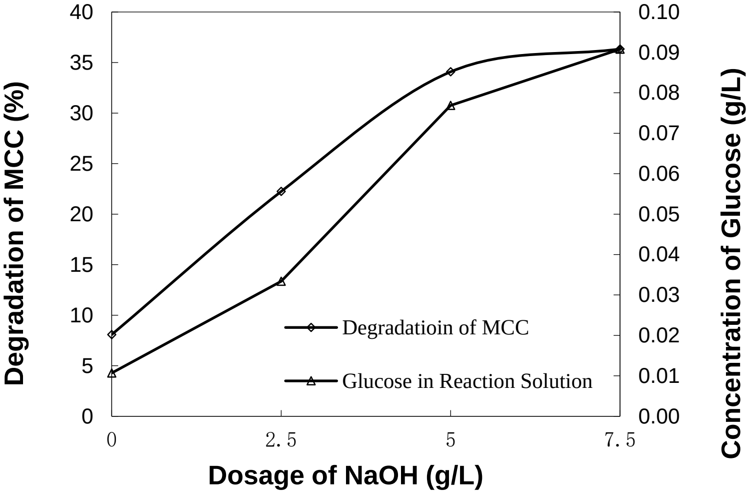

Fig. 3. Degradation of MCC and the concentration of glucose in the reaction solution as functions of the different dosage of NaOH. The reaction temperature was 90 °C, and the reaction time was 4 h.

Effect of the Dosage of NaOH on the Alkaline Degradation of MCC

Figure 3 shows that the dosage of NaOH had a great impact on the alkaline degradation of MCC and the production of glucose. With increasing dosage, the amount of degraded MCC and the glucose content in the reaction solution also increased. The amount of degraded MCC and the glucose content increased by 1.74% and 0.0139 g/L, respectively, when the dosage of NaOH increased from 20% to 30%.

Metal ions of the alkali solution existed in the form of hydrated ions, which penetrate into the crystalline region to react with the hydrogen bond of MCC. When part of the glycosidic bond split and a reducing end group was produced, a peeling reaction created glucose. During the first stage, with an increase in NaOH concentration, the amount of alkaline metal hydration ion rose, which accelerated the alkaline degradation of cellulose. However, when the dosage of NaOH was increased from 20% to 30%, the density of the ion was so big that the radius of the hydrated ion diminished, decreasing the destruction of MCC.

Effect of Metal Ions on the Alkaline Degradation of MCC

To explain the effect of the metal ions on the alkaline degradation of MCC, the dosages of K^+ and Mg^{2+} were varied. Their chemical valences are different. K^+ could weaken combination between cellulose by replacing the hydrogen of the hydrogen bond, while Mg^{2+} plays an opposite role (Huang *et al.* 2015). The result is shown in Fig. 4 and through infrared analysis. The degraded weight of MCC became higher with increasing K^+ dosage and prolonged reaction time. The degraded MCC was increased by 14.10% from 39.34% (9% K^+ dosage) to 34.48% (control) after reaction for 4 h. This result indicated that K^+ promoted the alkaline degradation of MCC.

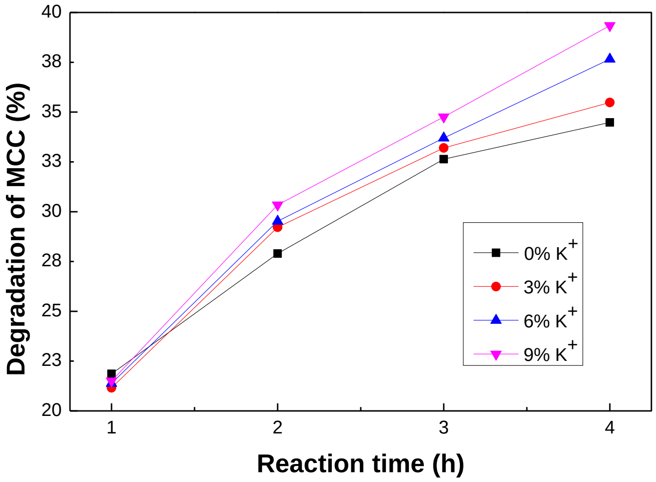

Fig. 4. Degradation of MCC in the reaction solution as functions of the different dosage of K^+. The concentration of NaOH was 5 g/L, and the reaction temperature was 90 °C.

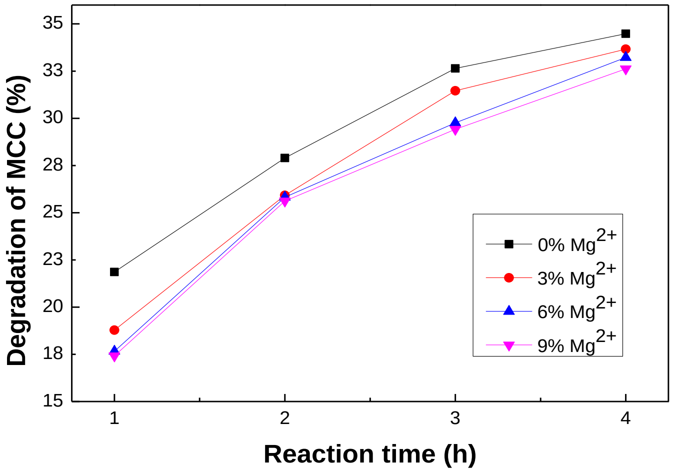

Fig. 5. Degradation of MCC in reaction solution as functions of the different dosage of Mg^{2+}. The concentration of NaOH was 5 g/L, and the reaction temperature was 90 °C.

Effect of Mg^{2+} on the alkaline degradation of MCC

As shown in Fig. 5, the degraded weight of MCC increased with the prolonging of reaction time and became lower with an increased Mg^{2+} dosage. This result indicated that Mg^{2+} inhibited the alkaline degradation of MCC. When the dosage of Mg^{2+} were 0% and 9%, the degraded MCC were 21.86% and 17.46% (after reaction for 1 h), 34.48% and 32.62% (after reaction for 4 h). This represents a decrease by 25.20% and 5.70%, respectively, which mean that the inhibition effect was more obvious in the early stage of the reaction.

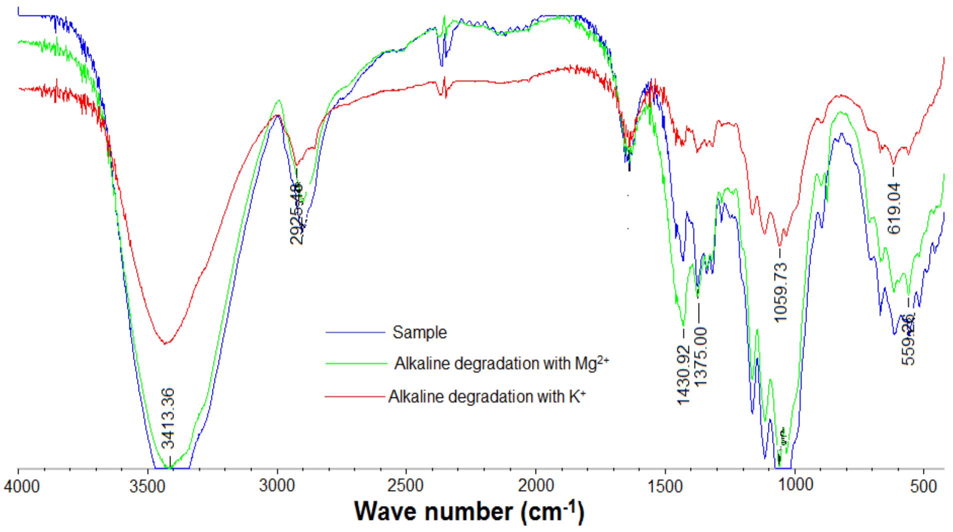

Fig. 6. The FTIR spectrum of MCC after alkaline degradation with and without Mg^{2+} and K^+

FTIR spectrum of MCC after alkaline degradation

Figure 6 compares the molecular structure changes of MCC with and without metal ions during alkaline degradation. In the FTIR spectrum, 3400 cm^{-1} expressed the hydroxyl absorption peaks in the intra- and inter- molecular hydrogen bonds (Dayal *et al*. 2013; Cozzolino *et al*. 2014; Rozenberga *et al*. 2016). The characteristic band at 2900 cm^{-1} was attributed to the C–H stretching vibration. The peak 1637 cm^{-1} represents the adsorbed water, and peaks 1432 cm^{-1} and 1164 cm^{-1} were characteristic of cellulose. The peak at 898 cm^{-1} represents the vibration absorption peaks of the β-2-glycosidic bond (Mecozzi *et al*. 2009).

Under the condition of adding Mg^{2+}, the absorption peaks located at 3400 cm^{-1}, 2900 cm^{-1}, and 898 cm^{-1} weakened, while compared with the condition without the metal ion, there was little change at 1637 cm^{-1}, 1432 cm^{-1}, and 1164 cm^{-1}. These phenomena indicated the fracture of intra-molecular hydrogen bonds, intermolecular hydrogen bonds, and β-2-glycosidic bonds. There was no change in the cellulose structure caused by the adsorbed water in the alkaline degradation.

The structure differences of MCC under the condition of adding K^+ without adding any other metal ion are shown in Fig. 6. The absorption peaks at 3400 cm^{-1}, 1637 cm^{-1}, and 898 cm^{-1}, represented an increase in intra-molecular hydrogen bonds, amount of water adsorbed, and β-2-glycosidic bonds, respectively. There was no change in the cellulose structure in the alkaline degradation by the analysis of the little change in 1432 cm^{-1} and 1164 cm^{-1}. Thus, K^+ and Mg^{2+} had opposite effects on the structure of MCC.

Glucose Concentrations in the Alkaline Degradation Reaction

As shown in Fig. 7, glucose was generated with the NaOH concentration, reaction temperature, and Mg^{2+} dosage of 5 g/L, 90 °C, and 1.5 g/L, respectively. In the alkaline degradation reaction, the glucose concentration became higher with increasing reaction time, which proved the alkaline degradation of MCC and the formation of glucose.

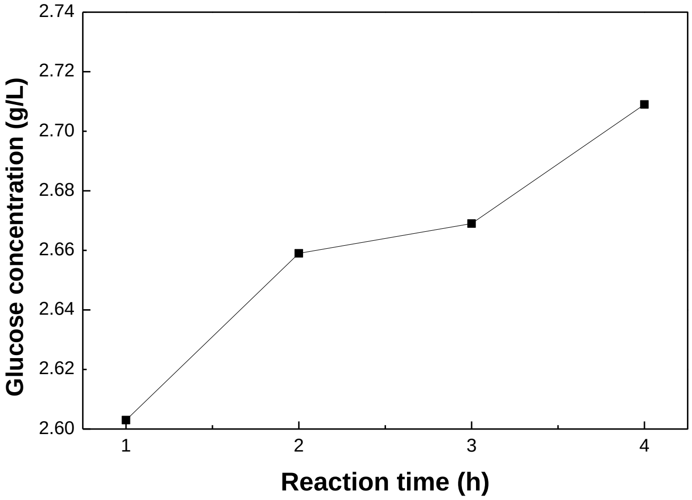

Fig. 7. The concentrations of glucose that were generated in the alkaline degradation of MCC; concentration of NaOH, the reaction temperature, and the dosage of Mg^{2+} were 5 g/L, 90 °C, and 1.5 g/L, respectively

CONCLUSIONS

1. The degree of alkaline degradation of MCC increased with an increase in the reaction temperature, reaction time, and the amount of alkali. When the reaction temperature was above 80 °C, the reaction time was above 2 h, or alkali content was below 20%, the rate of MCC degradation became slow. The growth relationship of the reaction rate was nearly linear when the alkali dosage was increased from 0 wt% to 20 wt%.
2. According to the change of the amount of MCC degraded in the reacting system, K^+ could promote the alkaline degradation of MCC, while Mg^{2+} could inhibit the alkaline degradation of MCC.
3. The theory of the alkaline degradation of MCC was further clearly expressed by an FTIR spectrum of MCC. The K^+ increased the intra-molecular hydrogen bonding, hydrogen bonds between the molecules, number of adsorbed water molecules, and the β-2-glycosidic bonds, while Mg^{2+} could reduce the intra-molecular hydrogen bonding, hydrogen bonds between the molecules, and β-2-glycosidic bonds. In other words, K^+ and Mg^{2+} had opposite impacts on alkaline degradation.
4. Under the conditions that the concentration of NaOH, the reaction temperature, and the dosage of Mg^{2+} were 5 g/L, 90 °C, and 1.5 g/L, respectively, the glucose was always produced, and the concentrations of glucose became higher with an increase in the reaction time in the alkaline degradation, which demonstrated the alkaline degradation of MCC and the formation of glucose.

ACKNOWLEDGMENTS

The authors thank Ms. Zhenzhen Wang for the FTIR analysis support and Dr. Jiayi Yang, who kindly reviewed this paper. The financial support from the Key Project of Natural Science Foundation of Tianjin (Grant No. 16JCZDJC37700) is also appreciated.

REFERENCES CITED

Askarieh, M. M., Chambers, A. V., Daniel, F. B. D., FitzGerald, P. J., Holtom, G. J., Pilkington, N. J., and Rees, J. H. (2000). "The chemical and microbial degradation of cellulose in the near field of a repository for radioactive wastes," *Waste Management* 20(1), 93-106. DOI: 10.1016/S0956-053X(99)00275-5

Berggren, R., Molin, U., Berthold, F., Lennholm, H., and Lindström, M. (2003). "Alkaline degradation of birch and spruce: Influence of degradation conditions on molecular mass distributions and fibre strength," *Carbohydrate Polymers* 51(3), 255-264. DOI: 10.1016/S0144-8617(02)00160-1

Butera, G., De Pasquale, C., Maccotta, A., Alonzo, G., and Conte, P. (2011). "Thermal transformation of micro-crystalline cellulose in phosphoric acid," *Cellulose* 18(6), 1499-1507. DOI: 10.1007/s10570-011-9590-3

Cozzolino, C. A., Cerri, G., Brundu, A., and Farris, S. (2014). "Microfibrillated cellulose (MFC): pullulan bionanocomposite films," *Cellulose* 21(6), 4323-4335. DOI: 10.1007/s10570-014-0433-x

Das Gupta, P. C., and Day, A. (1984). "Alkaline degradation of ramie (*Boehmeria nivea*) hemicellulose," *Cellulose Chemistry and Technology* 18, 79-82.

Dayal, M. S., Goswami, N., Sahai, A., Jain, V., Mathur, G., and Mathur, A. (2013). "Effect of media components on cell growth and bacterial cellulose production from *Acetobacter aceti* MTCC 2623," *Carbohydrate polymers* 94(1), 12-16. DOI: 10.1016/j.carbpol.2013.01.018

Eichhorn, S. J., and Young, R. J. (2001). "The Young's modulus of a microcrystalline cellulose," *Cellulose* 8(3), 197-207. DOI: 10.1023/A:1013181804540

El-Sakhawy, M., and Hassan, M. L. (2007). "Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues," *Carbohydrate Polymers* 67(1), 1-10. DOI: 10.1016/j.carbpol.2006.04.009

He, Y. L., Liao, X. X., and Huang, K. L. (2010). "Study process of microcrystalline cellulose," *Technology & Development of Chemical Industry* 39(1), 12-16. DOI：10.3969/j.issn.1671-9905.2010.01.005

Helmy, S. A. (1993). "Studies on the alkaline degradation of cellulose: Part II. Effect of the supermolecular structure of the pulp," *Polymer Degradation and Stability* 39(2), 159-162. DOI: 10.1016/0141-3910(93)90089-2

Huang, H., Cao, S. L., and Ma, X. J. (2015). "Effect of transition metal ions on the oxygen delignification of radiate pine kraft pulp," *Paper and Paper Making* 34(4), 10-17. DOI: 10.13472/j.ppm.2015.04.004

Greenfield, B. F., Hurdus, M. H., Pilkington, N. J., Spindler, M. W., and Williams, S. J. (1994). "The degradation of cellulose in the near field of a radioactive waste repository," *Materials Research Society Symposium Series* 333, 705-710. DOI: 10.1557/PROC-333-705

Kim, U, J., Isobe, N., Kimura, S., Kuga, S., Wada, M., Ko, J. H., and Jin, H. O. (2010). "Enzymatic degradation of oxidized cellulose hydrogels," *Polymer Degradation and Stability* 95(12), 2277-2280. DOI: 10.1016/j.polymdegradstab.2010.09.005

Klemm, D., Philipp, B., Heinze, T., Heinze, U., and Wagenknecht, W. (1998). *Comprehensive Cellulose Chemistry. Volume I: Fundamentals and Analytical Methods*, Wiley-VCH, Germany.

Kobayashi, S., Sakamoto, J., and Kimura, S. (2011). "In vitro synthesis of cellulose and related polysaccharides," *Progress in Polymer Science* 26(9), 1525-1560.DOI: 10.1016/S0079-6700(01)00026-0

Liu, M., Wang, H., Han, J., and Niu, Y. F. (2012). "Enhanced hydrogenolysis conversion of cellulose to C2–C3 polyols via alkaline pretreatment," *Carbohydrate Polymers* 89(2), 607-612. DOI: 10.1016/j.carbpol.2012.03.058

Mecozzi, M., Pietrantonio, E., and Pietroletti, M. (2009). "The roles of carbohydrates, proteins and lipids in the process of aggregation of natural marine organic matter investigated by means of 2D correlation spectroscopy applied to infrared spectra," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 71(5), 1877-1884. DOI: 10.1016/j.saa.2008.07.015

Northolt, M. G., Boerstoel, H., Maatman, H., Huisman, R., Veurink, J., and Elzerman, H. (2001). "The structure and properties of cellulose fibres spun from an anisotropic phosphoric acid solution," *Polymer* 42(19), 8249-8264. DOI: 10.1016/S0032-3861(01)00211-7

Pavasars, I., Hagberg, J., Borén, H., and Allard, B. (2003). "Alkaline degradation of cellulose: mechanisms and kinetics," *Journal of Polymers and the Environment* 11(2), 39-47. DOI: 10.1023/A:1024267704794

Rozenberga, L., Skute, M., Belkova, L., Sable, I., Vikele, L., Semjonovs, P., Saka, M., Puklisha, M., Paegle, L. (2016). "Characterisation of films and nanopaper obtained from cellulose synthesised by acetic acid bacteria," *Carbohydrate Polymers* 25(144), 33-40. DOI: 10.1016/j.carbpol.2016.02.025

Saqib, A. A. N., and Whitney, P. J. (2011). "Differential behaviour of the dinitrosalicylic acid (DNS) reagent towards mono- and di-saccharide sugars," *Biomass and Bioenergy* 35(11), 4748-4750. DOI: 10.1016/j.biombioe.2011.09.013

Suzuki, T., and Nakagami, H. (1999). "Effect of crystallinity of microcrystalline cellulose on the compactability and dissolution of tablets," *European Journal of Pharmaceutics and Biopharmaceutics* 47(3), 225-230. DOI: 10.1016/S0939-6411(98)00102-7

Teixeira, R. S, S., da Silva, A. S, A., Ferreira-Leitão, V. S., and da Silva Bon, E. P. (2012). "Amino acids interference on the quantification of reducing sugars by the 3, 5-dinitrosalicylic acid assay mislead carbohydrase activity measurements," *Carbohydrate Research* 363, 33-37. DOI: 10.1016/j.carres.2012.09.024

Yoon, J. J., Cha, C. J., Kim, Y. S., and Kim, W. (2008). "Degradation of cellulose by the major endoglucanase produced from the brown-rot fungus *Fomitopsis pinicola*," *Biotechnology letters* 30(8), 1373-1378. DOI: 10.1007/s10529-008-9715-4

Zaman, M., Xiao, H., Chibante, F., and Ni, Y. (2012). "Synthesis and characterization of cationically modified nanocrystalline cellulose," *Carbohydrate Polymers* 89(1), 163-170. DOI: 10.1016/j.carbpol.2012.02.066

Article submitted: October 6, 2016; Peer review completed: November 20, 2016; Revised version received and accepted: November 30, 2016; Published: January 4, 2017.
DOI: 10.15376/biores.12.1.1263-1272