CELLULOSE CHEMISTRY AND TECHNOLOGY

# PRODUCING BLEACHED MICROCRYSTALLINE CELLULOSE BY TWO-STAGE DILUTE ACID HYDROLYSIS

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This study investigates the process of producing microcrystalline cellulose (MCC) through two-stage acid hydrolysis with intermediate washing and removal of dissolved sugars. The temperature–time dependence shows fast xylose extraction in the initial phase of the process, while the glucose increases slowly and permanently over the period. After the second stage of hydrolysis, a cleaning effect and an increase in pulp brightness is observed. This method allows obtaining MCC, with high brightness and properties appropriate for usage in the pharmaceutical, cosmetics and food industries, as well as in the chemical industry, from paper grade pulp, which contains large amounts of hemicelluloses.

***Keywords***: brightness, microcrystalline cellulose, two-stage acid hydrolysis

## INTRODUCTION

Microcrystalline cellulose (MCC) is a partially depolymerised cellulose, with a low degree of polymerisation (DP). MCC is a white, odourless, non-toxic and biodegradable material in the form of powder.[1] Due to the properties resulting from its chemical nature, MCC is a multifunctional product with wide-spread and diverse applications, especially in the food, pharmaceutical and cosmetic industries.[2] There are different methods for producing MCC described in the literature, by the combination of chemical treatment with different other processes.[3,4] Some industrial production methods for MCC are based on acid and enzymatic hydrolysis, thermal explosion process and mechanical disintegration.[5-7] The acid hydrolysis process is preferred over treatments requiring longer reaction duration, moreover, it consumes a limited quantity of acid.[3,8] The acid selectively attacks the less ordered regions of the cellulose polymer chain, thereby exposing and freeing the crystalline sites that form crystallite aggregates, which constitute the MCC. The cellulose chain is tightly packed into a crystalline structure with extensive hydrogen bonding, which makes the cellulose microfibrils very resistant to acid treatment, in comparison with the hemicelluloses.[9] The glycosidic links in the amorphous domains break 1000-5000 times faster than the glycosidic linkages in the crystalline areas.[10] The acid hydrolysis product mixture (called hydrolysate) contains dissolved sugars and their derivatives. 5-Hydroxymethylfurfural (5-HMF) is formed as a product of glucose decomposition.[11] 5-HMF readily decomposes into levulinic and formic acids under conditions used in cellulose acid hydrolysis, and the decomposition rate is highly affected by increasing temperature.[12] Hemicelluloses degrade to form furfural, which is considered a valuable chemical. This process is followed by further decomposition into organic acids and condensation reactions into humin-like substances.[13] The degraded by-products must be fully removed and separated from the MCC by washing.

The classic process for MCC production is acid hydrolysis of purified cellulose, pioneered by Battista.[14] Cellulose is hydrolysed by boiling it in a 2.5 normal solution of hydrochloric acid, followed by mechanical treatment. Toshkov *et al.* developed a method using 1% sulfuric acid solution as hydrolysing medium and obtained a high yield, which decreased the aggregation by optimizing the pulping process.[15] Ha and Landi used optimized steam explosion to reduce the cost

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of the process, while maintaining or improving the quality of MCC.[16]

Residues from annual plants, such as rice and bean hulls, are interesting alternatives as cellulose sources for MCC preparation, as the obtained properties are similar to those of commercial MCC.[17,18] However, because of the specific pulping and bleaching treatment, there is a need for a more efficient and economical process. According to the AaltoCell™ process, microcrystalline cellulose can be effectively produced from fibrous cellulosic material by sulfuric acid hydrolysis at a high consistency of at least 8% and temperature of at least 80 °C, and the manufacturing process can be integrated into a kraft pulp mill.[19]

In order to obtain MCC for pharmaceutical applications from lower cost pulps, such as paper grade pulps, it is necessary that MCC should possess high brightness. The pentosans content in such pulps is significantly higher than in the dissolving pulps currently employed for this purpose. Because of a lot of caramelized sugar formations, the brightness of MCC from paper grade pulps is lowered significantly at the end of hydrolyses. Under optimized conditions, sugar caramelization could be limited if the sugar concentrations are lower. Normally, neutralization or alkalization of MCC before the next bleaching stage, preferably with hydrogen peroxide, is used for increasing brightness.[20]

The aim of this work was to develop a new more efficient production method for MCC with higher brightness, based on two-stage dilute sulfuric acid hydrolysis of bleached hardwood kraft pulp.

## EXPERIMENTAL

The hardwood bleached kraft pulp used in this study was provided by Svilosa AD, Svishtov. Its characteristics were determined according to standard analytical procedures. The ISO brightness of the pulp was 90% (ISO standard 2470-1:2016), the degree of polymerisation – 1200 (Ph. Eur.) and the pentosans content of 20% (TAPPI standard T 223 cm-10).

Dilute acid hydrolysis was performed in 2 L stainless steel laboratory autoclaves under the following conditions: the sulfuric acid charge – 0.5 and 2% on dry pulp; 10, 12.5 and 20% pulp consistency; hydrolysis temperature of 120 and 130 °C, reaction time at maximum temperature from 40 to 120 min. The pulp was fully washed with deionized water to a pH above 5 by multiple filtration runs on a Buchner funnel.

The degree of polymerisation of the MCC samples was measured according to the procedures described in the European Pharmacopoeia.[21] The MCC yield was analysed by gravimetrical determination. The average particle size of the MCC samples was determined by the laser diffraction method, using a Laser Particle Sizer Analysette 22 MicroTec Plus (Fritsch, Germany).

Liquid samples taken from the hydrolysis were centrifuged for 4 min at 8490 g (BOECO centrifuge Microspin 12) and then filtered through a 0.2 μm CA membrane (NML 16534). The content of sugars released during the acid hydrolysis was assessed on a Dionex HPLC system (Dionex Inc., CA, USA), according to the NREL Technical Report.[22] The separation was performed on a Hi-Plex H column, 7.7 mm × 300 mm (Agilent Technologies, USA) and quantified on a Shodex RI-101 RI detector (Showa Denko KK, Kawasaki, Japan). Ultrapure water (18.2 MΩ·cm resistivity at 25 °C) produced by a Simplicity® water purification system (Merck KGaA, Darmstadt, Germany) was used as mobile phase at a flow rate of 0.5 mL $min^{-1}$ (at 65 °C). The results were evaluated by Chromeleon 6.80 software.

## RESULTS AND DISCUSSION

The current investigations show that, in the initial stage of the dilute acid hydrolysis for producing MCC, mainly hemicelluloses (3-5% xylose) are dissolved, and to a lower extent, cellulose (up to 1.2% glucose). A pulp cleaning effect is observed and, as a result, pulp brightness increased by nearly 1.5% (Fig. 1a and b). This is due to the removal of the xylan-related residual chromophores from the pulp by hydrolysis.

The high pentosans content in bleached hardwood kraft pulp generates a lot of xylose in the next stage of the process (Table 1). Under these conditions, the formation of furfural and furfural-derived chromophores also takes place. Due to this, the brightness of the microcrystalline cellulose decreases significantly at the end of the hydrolysis process. A linear relationship between MCC brightness and the formation of furfural during acid hydrolysis is obtained, thus confirming the fact that furfural-derived chromophores are responsible for the decreased brightness (Fig. 2).

In biorefinery scenarios, the furfural and 5-HMF formed from xylose and glucose, respectively, are the most well-known example.[23,24] These conversions are always accompanied by the formation of black condensation products, which reduce the yields and cause separation and purification problems.

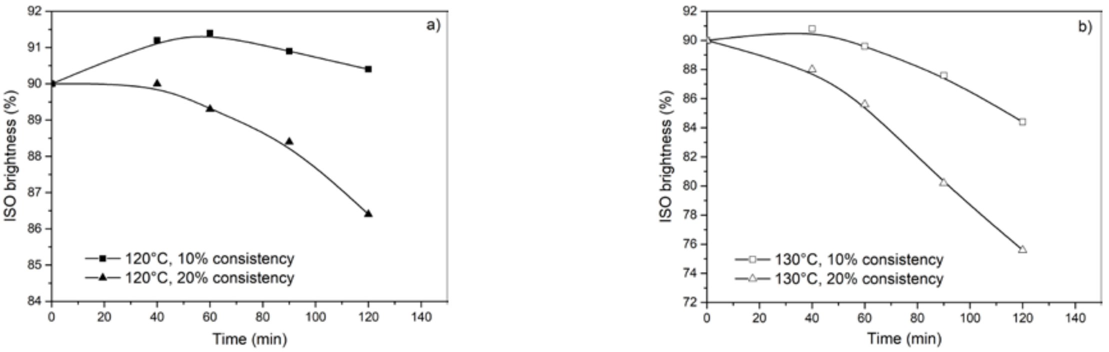

Figure 1: Kinetic curves of pulp brightness in the first acid hydrolysis stage: a) at 120 °C; b) at 130 °C

Table 1
First stage sulfuric acid hydrolysis at a temperature of 130 °C and acid charge of 2%

| Pulp consistency (%) | Hydrolysis duration (min) | Yield (%) | Glucose (%) | Xylose (%) | Furfural (%) | DP | MCC ISO brightness (%) | Average particle size (µm) |
|---|---|---|---|---|---|---|---|---|
| 10 | 40 | 95.5 | 0.29 | 3.04 | 0.01 | 400 | 90.7 | 69.1 |
| 10 | 60 | 94.4 | 0.46 | 3.65 | 0.04 | 363 | 89.5 | 58.7 |
| 10 | 90 | 93.1 | 0.81 | 4.52 | 0.08 | 319 | 87.5 | 42.0 |
| 10 | 120 | 91.9 | 1.16 | 5.13 | 0.14 | 299 | 84.4 | 41.8 |
| 12.5 | 120 | 89.5 | 1.52 | 5.74 | 0.22 | 283 | 83.6/82.4(a) | 41.3 |
| 12.5 | 150 | 85.81 | 2.38 | 7.34 | 0.34 | 268 | 80.7 | 37.3 |

(a) brightness after partial washing

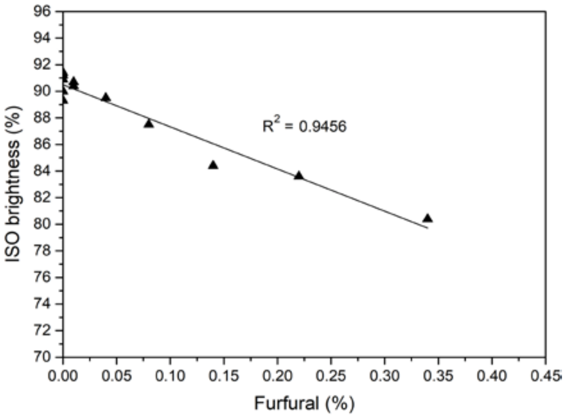

Figure 2: Correlation between pulp brightness and amount of furfural in the first stage of sulfuric acid hydrolysis (temperature – 120 and 130 °C, reaction time – 40-120 min, consistency – 10 and 12.5%)

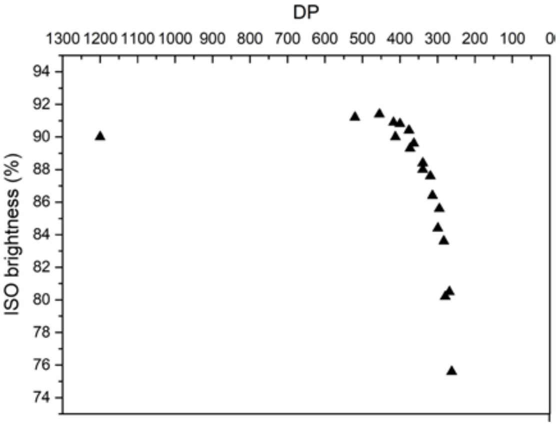

Figure 3: Correlation between pulp brightness and DP in the first stage of sulfuric acid hydrolysis (temperature – 120 and 130 °C, reaction time – 40-120 min, consistency – 10, 12.5 and 20%)

These dark by-products are usually denoted as humins and are structurally completely different from humic matter in soil. Humins are formed by side reactions of furans, exactly like the HexA-derived chromophores.[21] Because of the formation of humins during acid hydrolysis intended for producing MCC, the kinetic curves of pulp brightness pass through a maximum, and the dark colour of MCC depends on the temperature, reaction time and acid concentration used (Fig. 1).

A correlation between pulp brightness and DP is found in dilute sulfuric acid hydrolysis, which is common and independent of the temperature, reaction time, pulp consistency and, respectively, acid concentration (Fig. 3). This is an indication of the dependence of the humins formation during the microcrystalline cellulose production on the degree of pulp hydrolysis. This correlation also shows that in one step acid hydrolysis, the obtained MCC, with a DP below 300, will always possess low pulp brightness, regardless of the hydrolysis conditions.

Two-stage acid hydrolysis is a solution to that brightness problem. Due to the removal of dissolved sugars and by-products by washing, the possibility of furfural and humins formation is minimized under these relatively mild conditions in the second stage of hydrolysis, and thus, the brightness of MCC remains very high until the end of the process.

Table 2 presents the results of the two-stage acid hydrolysis with short first stages, of 40 and 60 min. The duration of the first stage corresponds to the established maximum brightness on the kinetic curves (Fig. 1). By extending the second stage of acid hydrolysis, MCC with high brightness and the desired DP can be obtained.

Table 2
Second stage sulfuric acid hydrolysis (after 40 and 60 min first stage) at temperature 130 °C and acid charge 2%

| First stage duration (min) | Second stage duration (min) | Second stage pulp consistency (%) | Second stage yield (%) | Total yield (%) | Second stage glucose (%) | Second stage xylose (%) | Second stage furfural (%) | DP | MCC ISO brightness (%) | Average particle size (µm) |
|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 60 | 20 | 93.9 | 89.7 | 1.51 | 3.86 | 0.00 | 278 | 89.9 | 38.9 |
| 60 | 60 | 20 | 95.1 | 89.8 | 1.11 | 2.65 | 0.00 | 275 | 89.2 | 38.0 |
| 60 | 90 | 10 | 93.1 | 88.4 | 0.88 | 2.42 | 0.04 | 268 | 90.1 | 38.8 |
| 60 | 120 | 10 | 91.9 | 88.2 | 1.00 | 2.43 | 0.05 | 264 | 90.0 | 39.0 |

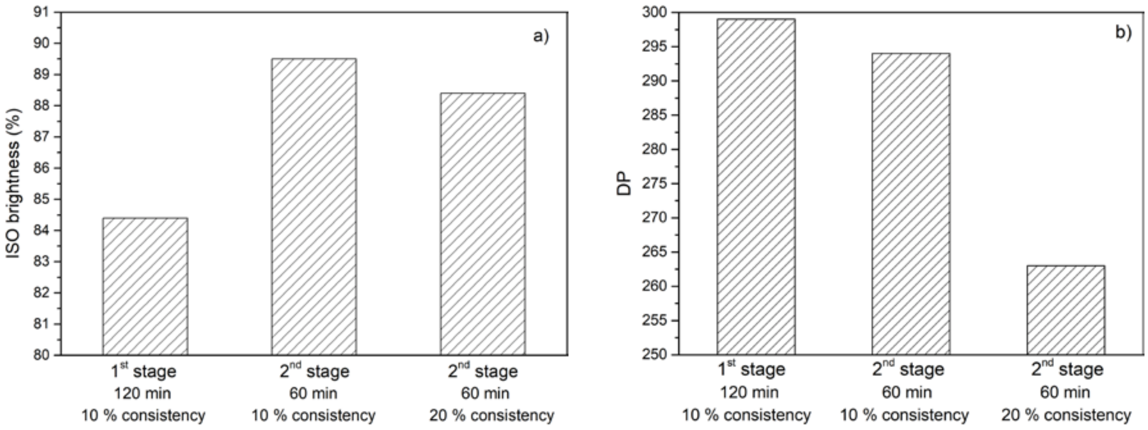

Figure 4: Effect of second stage sulfuric acid hydrolysis at a temperature of 130 °C and 2% acid charge; a) MCC brightness; b) DP of MCC

The results presented in Figure 4a show that high brightness of MCC is also achieved after two-stage acidic hydrolysis with a prolonged first stage, in the case of low intermediate brightness. In this situation, the second stage of acid hydrolysis has a cleaning effect, where the absorbed chromophore structures are removed from the pulp and no further bleaching is required. A certain decrease in the final DP of MCC at higher pulp consistency in the second stage has been also found (Fig. 4b).

A reaction temperature of 130 °C is required for an optimal cleaning effect in the second hydrolysis stage. A reduction in pulp brightness is observed at a higher temperature, because of increasing humins formation. The degree of polymerisation of MCC also decreases under these conditions (Fig. 5a).

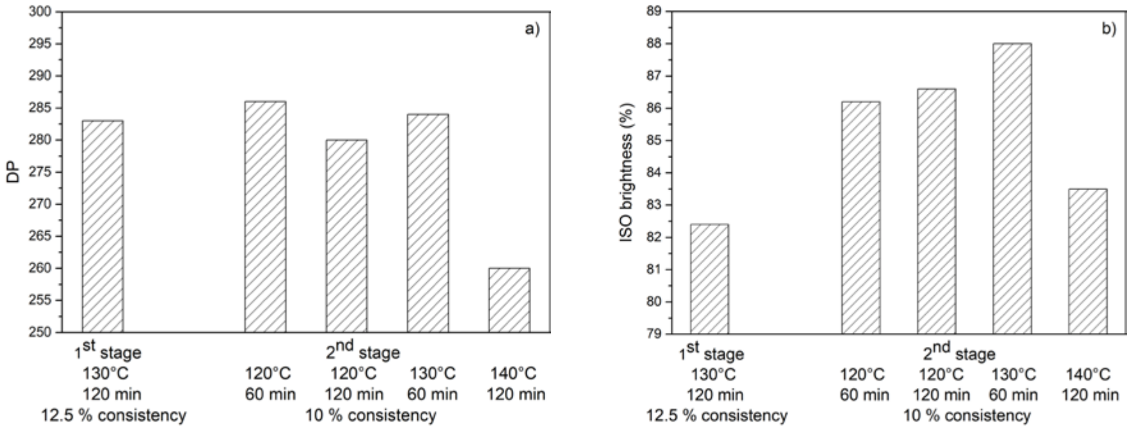

Figure 5: Effect of second stage sulfuric acid hydrolysis at 0.5% acid charge and partial washing between the stages; a) DP of MCC; b) MCC brightness

MCC brightness of 88% can be achieved in the case of 0.5% sulfuric acid charge in the second step with partial washing between the stages (Fig. 5b). The filtrate from the second hydrolysis stage can be reused in the first stage, with the possibility of integrating the process in a kraft pulp mill and reducing the final product price.

Another advantage of two-stage hydrolysis, compared to the one-stage process, is the observed better particle uniformity of MCC (Table 2).

## CONCLUSION

Two-stage dilute sulfuric acid hydrolysis allows the production of microcrystalline cellulose with high brightness, better particle uniformity and a desirable degree of polymerisation, from hardwood bleached kraft pulp.

Cleaning effects and increasing pulp brightness have been established, in the initial step of acid hydrolysis due to the dissolution of the residual chromophores absorbed on the xylan, and in the second hydrolysis stage due to the removal of the absorbed humins.

The formation of furfural and humins was minimised during the two-stage acid hydrolysis due to the removal of dissolved sugars by washing. Thus, the brightness of microcrystalline cellulose remained very high and no further bleaching was required.

Partial washing between the stages and a low sulfuric acid charge in the second step are sufficient for high MCC brightness. The filtrates from the hydrolysis stages can be reused and integrated into kraft pulp processes.

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