

Effect of Mild Acid Hydrolysis Parameters on Properties of Microcrystalline Cellulose

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The effects of mild kraft pulp hydrolysis conditions (reaction time, temperature, pulp consistency, and acid dosage) with sulfuric acid (H₂SO₄) on the properties of microcrystalline cellulose (MCC) were investigated. The degree of polymerization (DP) of cellulose rapidly decreased at the initiation of hydrolysis and leveled off after a certain reaction time, depending on the hydrolysis conditions. The intensity of the hydrolysis treatment greatly affected the cellulose particle size. Compared to the intensive treatment, the mild conditions resulted in a broader particle size distribution, while smaller particles with a narrow size distribution were obtained under severe conditions. However, the particle size leveled off at a hydrolysis factor (P-factor) of 300. The results suggest that after a certain P-factor (300), severe hydrolysis conditions have no advantage over mild ones as related to the MCC particle properties. Because of favourable reaction conditions (short delay time, moderate temperature, and small amounts of chemicals), this method can be implemented on an industrial scale in a chemical pulp mill.

Keywords: Microcrystalline cellulose; Acid hydrolysis; Degree of polymerization; Particle size

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INTRODUCTION

The global market size of microcrystalline cellulose (MCC) is more than 100,000 tons and growing approximately 5% annually (Ciechanska *et al.* 2010). Pharmaceuticals (stabilizing, texturing, and tableting) and food applications (food and beverage texturing agents and dietetic substances) comprise the largest market areas for MCC. In smaller quantities, it is used for oil drilling, paints, cosmetic products, heat shields, and flame-resistant boards (Tuason *et al.* 2009).

MCC is a powder-like cellulose product that can be prepared from all forms of natural celluloses, alkali celluloses, regenerated celluloses, and even a low degree of substitution cellulose derivatives (Battista and Smith 1962). The Food and Agriculture Organization of the United Nations Document Repository (FAO 1996) of the United Nations defines MCC as “purified, partially depolymerized cellulose prepared by treating alpha-cellulose, obtained as a pulp from fibrous plant material, with mineral acids. The degree of polymerization (DP) is typically less than 400. Not more than 10% of the material has a particle size of less than 5 µm”.

Battista and Smith (1962) defined MCC as “a mechanically disintegrated D.P. cellulose, where level-off D.P. (or D.P. cellulose) is defined as the product resulting from, or equivalent to, the hydrolysis of purified cellulose after 15 minutes in 2.5 N hydrochloric acid (HCl) at 105 ± 1° C”.

In cellulose acid hydrolysis research, Battista (1950) and Battista and Smith (1962) observed the following:

1. During hydrolysis, the cellulose degree of polymerization levels off at a higher value as the temperature decreases (Fig. 1).

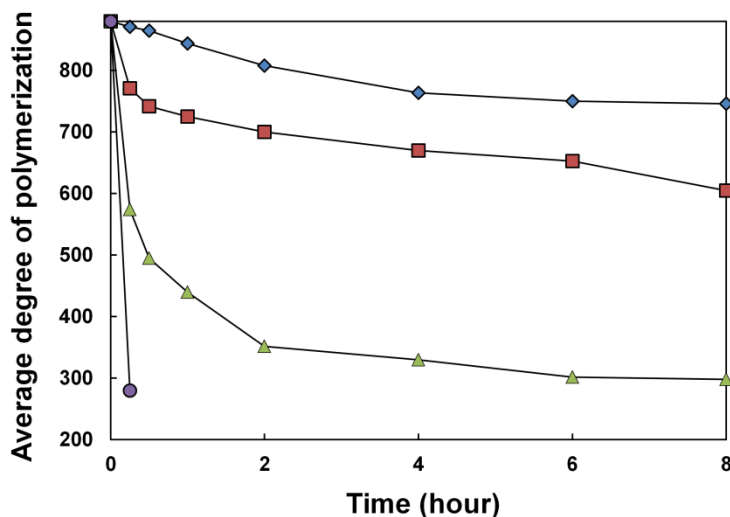


Fig. 1. Hydrolysis of cotton linter pulps with 5N HCl at 5 °C (◆), 18 °C (■), 40 °C (▲), and 100 °C (●). Replotted from Battista (1950) for the sake of comparison

2. Yield loss of hydrolysis and degree of polymerization depend on the raw material.
3. As acid hydrolysis proceeds and the degree of polymerization levels off, mild acid hydrolysis gives a higher yield as compared to severe hydrolysis, even though treatment time was longer under the mild conditions.
4. Carrying out the hydrolysis in two stages, using mild conditions in the first (pre-treatment) stage and harsh conditions in second stage, allows a reduction in the entire yield loss as compared to one-stage hydrolysis under harsh conditions from the start.
5. Drying of hydrolyzed cellulose produces a flour of colloidal size.

Since that time, the commercial methods to produce MCC (Toshkov *et al.* 1976; DeLong 1986; Milford *et al.* 2001; Jollez *et al.* 2002; Mattheson *et al.* 2002; Schaible and Brinkman 2003; Nguyen 2004; Ioelovich and Leykin 2005; Schaible and Sherwood 2005) have been based on the innovation of Battista *et al.* (1961) or its modifications. No further basic phenomena of significance for MCC manufacturing via acid hydrolysis have been discovered to date.

Another way to produce MCC is via enzymatic hydrolysis, which enables the use of bleached kraft pulp as a raw material. The disadvantage of enzymatic hydrolysis has a very long retention time (> 10 h rather than 24 h or more (Braunstein *et al.* 1994)), which prevents its high volume manufacturing. Using the existing acid hydrolysis for MCC manufacturing, the main challenges are related to high acid consumption which lead to economic (high production costs) and environmental (high chemical oxygen demand (COD) concentration in effluents) problems.

This paper investigates and presents the effects of the technological process parameters on the product properties obtained with the improved method to produce MCC with sulfuric acid (Dahl *et al.* 2011). Very low concentrations of acid were employed compared to the existing methods. In addition, the new approach enables the use of paper pulp as a raw material.

EXPERIMENTAL

Materials

Never-dried bleached softwood kraft pulp supplied from an Eastern Finnish pulp mill was used as the cellulose raw material. The viscosity of the pulp (SCAN standard 1999) was 917 mL/g, the degree of polymerization (see Analyses Section) was 2673, and the brightness (ISO) was 89%.

The hydrolysis agent was H₂SO₄ (95-98% analysis quality; Merck; Germany), which was diluted with deionized water to a 1.0 M concentration for further use. In the hydrolysis experiments, deionized water was used.

Methods

Hydrolysis Experiments

Experiments were carried out in an air bath digester consisting of six tube-like reactors with a total volume of 2.5 dm³. The conditions for acid hydrolysis are listed in Table 1.

Table 1. Acid Hydrolysis Conditions

Consistency (%)	H ₂ SO ₄ dosage* (%)	Hydrolysis time** (min)	Hydrolysis temperature (°C)
10.0-25.0	0.5-1.5	0.0-1440.0	120.0-160.0
* acid amounts have been calculated for oven dry cellulose weights			
** pre-heating and heat-up period excluded			

For each hydrolysis, pulp (100 g of oven dry weight) was mixed with various amounts of H₂SO₄ and deionized water. After pre-heating to 50 °C (10 to 15 min), the reactors were brought up to the hydrolysis temperature at a speed of 1 °C/min and kept there for various periods of time. Hydrolysis was stopped by cooling the reactor vessel in a cold water bath for 15 min.

After cooling, the hydrolysis liquid was filtered, and the solid residue was washed with 1 L of deionized water for 1 min. The washing procedure was repeated three times. Liquid from the solid residue was separated using a laundry centrifuge (UPO, Finland) at 4500 rpm with a filter bag (max. capacity 3.0 kg).

Analyses

Raw material and hydrolyzed solid residue brightness were measured according to the standards (SCAN standard 1993; 1995) with the exception that filter paper (diameter 110 mm; Whatman 4; USA) was used rather than standard wire. Viscosities were measured according to the standard (SCAN standard 1999) and the degree of polymerization was

calculated according to the Mark-Houwink equation as guided by the corresponding SCAN standard (1988). The hydrolysis yield was determined gravimetrically.

The particle size distribution of the hydrolyzed solid residue was measured by laser diffraction with a Mastersizer 2000 (Malvern Instruments Ltd; United Kingdom) equipped with a Hydro 2000MU wet dispersion unit. The size distribution d50 value was used as an average particle size. The analyses were carried out using distilled water as the dispersion medium and applying Fraunhofer parameters (refractive index (RI) 1.33 for water and RI 1.59 and absorption index 0.01 for solid residue material).

Approximately 0.5 to 1.0 g of solid residue material was dispersed in 25.0 mL of distilled water. The stirring rate of the dispersion unit was adjusted to 800 rpm. The sample was treated ultrasonically (amplitude 39% and 20 Hz) for 60 seconds prior to particle size measurement with an Ultrasonic VCX 750 (Sonics & Materials, Inc.; USA). Approximately 5 mL of the stirred and sonicated sample was pipetted to the dispersion unit. Particle sizes were measured in three sequential measurements at 60-s intervals. The background was measured with distilled water each time prior to measuring the sample. The measuring time for each background and sample measurement was 5 s and carried out at room temperature (22 °C).

The X-ray diffraction (XRD) of samples was analyzed with X'Pert PRO MPD Alpha-1 (PANalytical; Holland) diffractometer using CuK α radiation source ($\lambda = 0.154056$ nm) operating at 45 kV and 20 mA. The used step size was 0.026°, counting time was 48 s, and the 2θ range was 5 to 70°.

The crystallinity index was calculated with two different methods: peak height and deconvolution. In peak height method crystallinity index was calculated from XRD data according equation by Segal *et al.* (1959):

$$CI = 100 \times \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

where CI is the crystallinity index, I_{002} is the intensity peak of crystalline region, and I_{am} is the intensity peak of amorphous region.

In the deconvolution method, peaks were separated from XRD data using a least-square profile program Peakfit (Systat Software Inc.; USA) assuming Gaussian function for each peak. Crystallinity index was calculated by dividing all crystalline peak areas with total area (Park *et al.* 2010).

P-factor calculation

The intensity of the hydrolysis treatment determined by time and temperature can be expressed as a single variable, the hydrolysis factor (P-factor), which allows the comparison of hydrolysis at different temperatures, *e.g.*, (Sixta 2006):

$$P\text{-factor} = \int_{t_0}^t \frac{k_{H,t}}{k_{100^\circ\text{C}}} \cdot dt = \int_{t_0}^t \text{Exp} \cdot \left(40.48 - \frac{15106}{T} \right) dt \quad (1)$$

where t is the reaction time in hours, T is the temperature in Kelvin, and k is the rate constant. The P-factors were calculated from the reaction time and reaction temperature data according to Eq. 1 using 125.6 kJ/mol (Sixta 2006) as the activation energy.

RESULTS AND DISCUSSION

Degree of Polymerization and Viscosity

During the first 2 h, the hydrolysis resulted in a significant reduction in the degree of cellulose polymerization, which leveled off with time (Fig. 2).

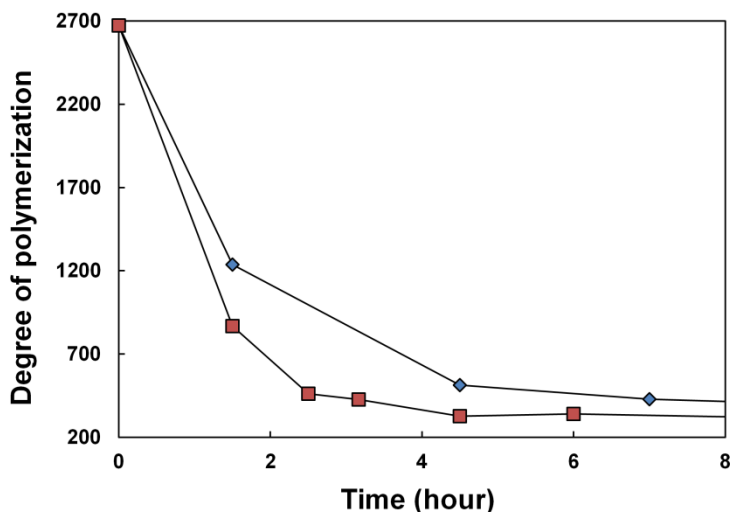


Fig. 2. Degree of polymerization as a function of hydrolysis time. Consistency 10% (◆) and 25% (■); temperature 140 °C, and H₂SO₄ dosage 0.5%

The same tendency was noted by Battista (1950), as shown in Fig. 1. Likewise, intrinsic viscosity decreased to level off with hydrolysis time (Fig. 3).

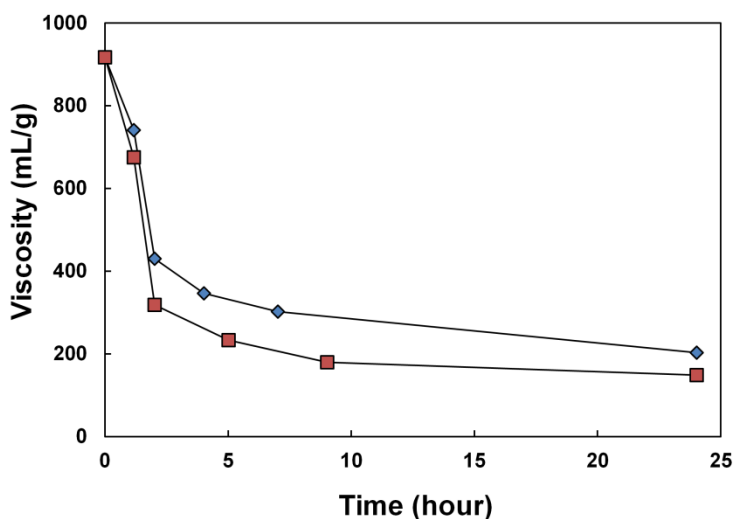


Fig. 3. Intrinsic viscosity of hydrolysis solid residue as a function of hydrolysis time. Consistency 10% (◆) and 25% (■); temperature 120 °C, and H₂SO₄ dosage 0.5%

Similarly, Håkansson and Ahlgren (2005) showed a decrease in intrinsic viscosity of a mixed hardwood pulp as a function of hydrolysis time under different hydrolysis

conditions. Battista (1950) has shown that by using the degree of polymerization-time data (expressed as $1/\eta$ vs. t), relative hydrolysis rate constants may be calculated by adapting Ekenstam's equation. Relative energies of activation, E_r , may be calculated by adapting the classical Arrhenius equation to calculate relative hydrolysis time constants, K , for samples having similar original and leveling-off degrees of polymerization at two different temperatures.

Yield

The weight loss during hydrolysis was found to be dependent on a combination of the rate at which hydrolysis proceeds and the crystallization and crystal growth that occurs simultaneously with the hydrolysis.

Concerning the reaction mechanism, Battista (1950) concluded that mild hydrolysis conditions, during which 1,4 glycosidic bonds are split at a relatively slow rate, favor crystal growth and the crystallization of long-chain segments that are acid-insoluble and resistant to further rapid hydrolysis. Severe hydrolysis, on the other hand, during which available 1,4 glycosidic bonds are split rapidly, results in the crystallization of very short-chain segments, giving rise to crystalline nuclei that are acid-soluble and more readily removed during the hydrolysis.

The yield of hydrolysis with different circumstances is shown in Fig. 4.

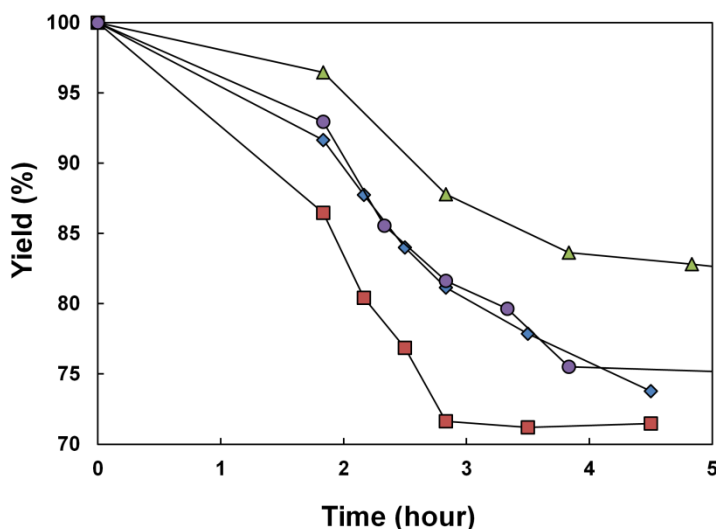


Fig. 4. Yield of cellulose as a function of hydrolysis time. (◆); Consistency 10%, temperature 160 °C, and H₂SO₄ dosage 1.5%, (■); Consistency 25%, temperature 160 °C, and H₂SO₄ 1.5%, (▲); Consistency 25%, temperature 140 °C, and H₂SO₄ dosage 1.5%, (●); Consistency 25%, temperature 160 °C, and H₂SO₄ dosage 0.5%

The yields were clearly leveling off, and the hydrolysis rate became higher with the higher consistency, temperature, or dosage. The time and the temperature of hydrolysis, as well as the H₂SO₄ dosage, were found to be the key factors of the MCC isolation process.

An apparent interaction between the acid concentration and the time of hydrolysis should be considered. It can be expected that an increase of hydrolysis temperature, acid concentration, and hydrolysis time will have a positive effect on the MCC size reduction, though at the expense of the yield (Battista 1950).

Further hydrolysis is expected to lead to even smaller particles. For example, using MCC as a starting material with a H₂SO₄ concentration of 63.5% (w/w), it was possible to obtain cellulose nanocrystals/whiskers with a length between 200 and 400 nm and a width less than 10 nm in approximately 2.0 h with a yield of 30.0% (Bondeson *et al.* 2006).

Pirani and Hashaikh (2013) attempted to recover and utilize the hydrolyzed regions of cellulose as a byproduct after H₂SO₄ hydrolysis. The acid hydrolyzed amorphous regions were separated and then recovered (regenerated) into solid particles, which showed that the recovered material is characteristic of cellulose II. The achieved yield values were approximately 61% for the cellulose I crystalline portions and approximately 21.7% for the recovered material (cellulose II).

Crystallinity indexes

It could be expected that the amorphous portion of cellulose, holding cellulose crystallites, would dissolve. The individual crystallites would be released in the course of acid hydrolysis, in accordance with the mechanism described by Battista (1950). However, the crystallinity measurements with X-ray diffraction revealed no significant change in crystallinity indexes between raw material and hydrolyzed samples (Table 2).

Table 2. Crystallinity Indexes of Raw Material and Hydrolyzed Samples Calculated with Two Methods (Peak height and deconvolution)

Hydrolysis time* (min)	Degree of polymerization	Yield (%)	CI _{Peak height} (%)	CI _{Deconvolution} (%)
Raw material	2673	100.0	77.9	50.1
0	1040	95.4	78.4	50.3
30	640	94.2	77.4	48.5
130	516	92.3	76.0	48.4
240	446	89.1	75.9	50.1
300	390	88.3	76.1	48.9
420	354	84.8	78.7	49.0
* pre-heating and heat-up period excluded (See materials section) 140 °C; consistency 10%; and H ₂ SO ₄ dosage 1.5%				

No significant difference in crystallinity between raw material and hydrolyzed cellulose samples could be detected (Table 2). Similarly, no such differences have been detected by Tolonen *et al.* (2011). A tentative explanation would be that two counter mechanisms are at operation: a) the dissolution of amorphous part and releasing individual crystallites, thus increasing the crystallinity; and b) hydrolysis of the crystalline part, leading to the decrease in crystallinity. Sun *et al.* (2008) arrived at a similar conclusion.

The crystallinity indexes in this study lay within the range of crystallinity indexes reported for Avicel (Park *et al.* 2010). These authors analyzed extensive literature data on crystallinity index measurements of the same commercial MCC product Avicel PH-101 and illustrated that the obtained cellulose crystallinity index results depend greatly on the XRD instruments and on the computation methods employed. Thus, the measured crystallinity values are comparable within the given study only.

An example of MCC XRD spectra obtained in this study is shown in Figure 5.

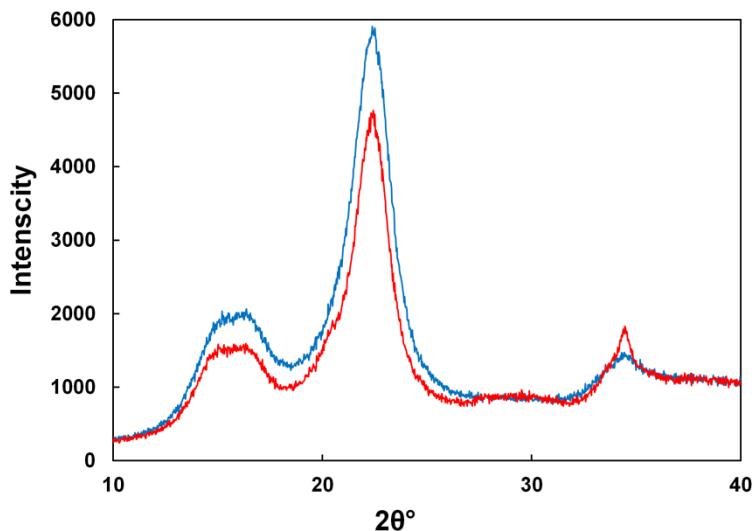


Fig. 5. XRD spectra of raw material (—) and 420 min hydrolyzed sample (—); Temperature 140 °C, consistency 10%, and H₂SO₄ dosage 1.5%

The intensity is somewhat higher for raw material than for hydrolyzed sample.

Brightness

The intensity of the hydrolysis treatment greatly affects the brightness of the solid residue. As shown in Fig. 6, the brightness decreases as the P-factor increases.

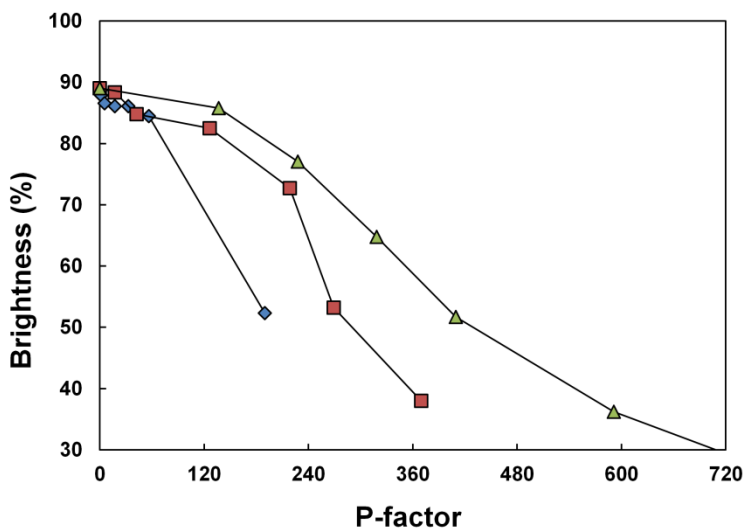


Fig. 6. ISO brightness as a function of P-factor. Hydrolysis temperature levels 120 °C (◆), 140 °C (■), and 160 °C (▲); H₂SO₄ dosage 1.5% and consistency 10%

With longer hydrolysis times, the solid residue becomes brown in color, with a pronounced caramel scent. Liavoga *et al.* (2007) and Ruiz *et al.* (2011) noted a similar smell and darkening with acid hydrolysis of wheat straw. This observed phenomenon is

due to dehydration and condensation reactions (caramelization), which carbohydrates undergo in acid media under elevated temperatures (Hodge 1953; Ledl and Schleicher 1990; Lichtenthaler 2011).

For industrial applications requiring high brightness, the hydrolysis conditions can be chosen to minimize the brightness loss so the brightness reversion will remain at an acceptable level. However, to attain high brightness of MCC (> 90 ISO%), the hydrolyzed solid residue can be bleached with an oxidative agent such as ozone, oxygen, or peroxide.

Particle Size

The intensity of hydrolysis greatly affects the cellulose particle size. Figure 7 shows the effect of the P-factor on the average particle size.

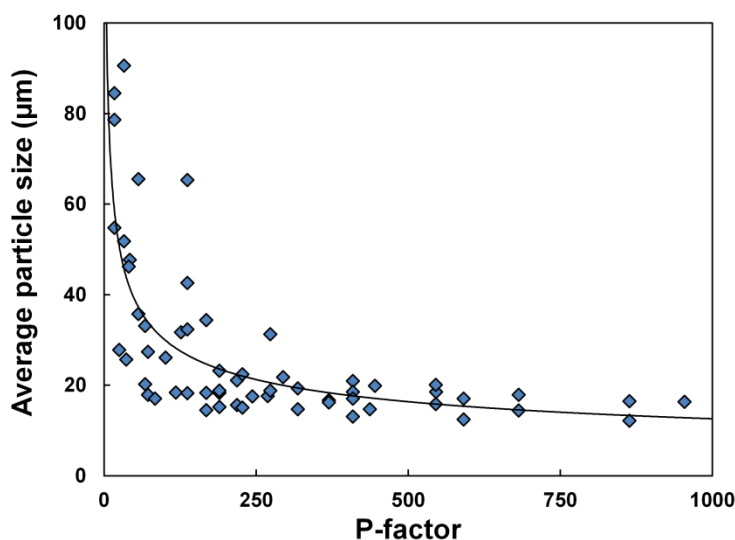


Fig. 7. Average particle size as a function of the P-factor (all hydrolysis test points, see Table 1).

Mild hydrolysis conditions result in a broad size distribution, whereas severe treatment yields smaller particles with the average size levelling off already at P-factor 300. This indicates that more intensive acid hydrolysis (up to P-factor 1000) provides no further particle size reduction. Thus, an important conclusion is drawn: using severe hydrolysis conditions has no advantage over mild treatment, and the sufficient P-factor lies under 300.

The degree of polymerization correlates well ($R^2=0.96$) with the average particle size data, as demonstrated in Fig. 8.

One must bear in mind that using different acids also affects the MCC properties. As shown by Araki *et al.* (1998), the H_2SO_4 -treated and HCl-treated samples had similar particle sizes and shapes when observed by electron microscopy. However, conductometric titration of suspensions revealed that the H_2SO_4 -treated sample had a surface charge of 84 m-equiv kg^{-1} dry material due to the introduction of sulfate groups, while that of the hydrochloric acid-treated sample was undetectable (Araki *et al.* 1998). This resulted in different viscosity behavior. The H_2SO_4 -treated suspension showed no time dependence in viscosity, while the hydrochloric acid-treated suspension was thixotropic at concentrations greater than 0.5% (w/v) and anti-thixotropic at concentrations less than 0.3%.

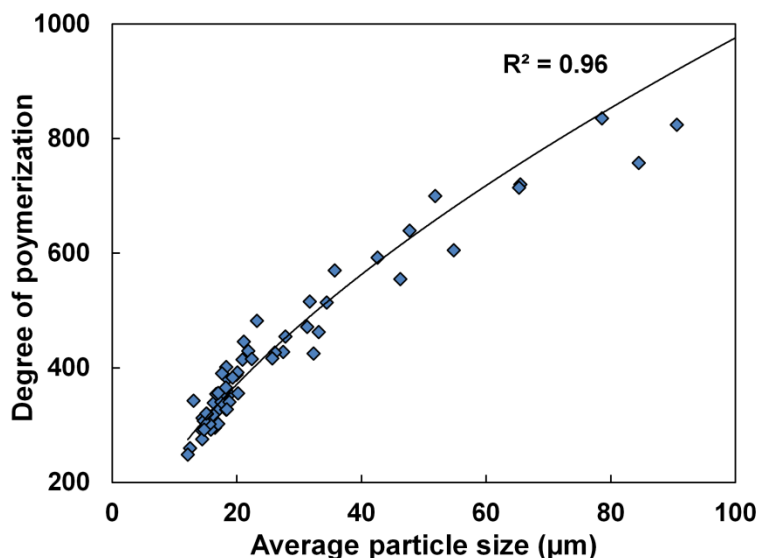


Fig. 8. Degree of polymerization as a function of average particle size (all hydrolysis test points, see Table 1.)

CONCLUSIONS

1. Fine cellulose crystallites can be produced and isolated under mild hydrolysis conditions (P-factor 300). More intensive acid hydrolysis (up to P-factor 1000) provides neither a further reduction in particle size nor a further decrease in degree of polymerization.
2. Using severe hydrolysis conditions has no actual advantage over using mild conditions, and the sufficient P-factor for fairly good control of particle size is under 300.
3. The particle size and DP of MCC can be controlled with sufficient accuracy by varying temperature, time, consistency, and acid dosage during mild acid hydrolysis.
4. Short delay time, moderate temperature, and low reagent consumption enable MCC manufacturing on a large scale with substantial energy saving using known process technology. This enables process integration in a chemical pulp mill.

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