Bulgarian Chemical Communications, Volume 58, Issue 2 (pp. 189-192) 2026 DOI: 10.34049/bcc.58.2.NCC02

Temperature-time and concentration dependences of mild dilute acid hydrolysis

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Received: December 04, 2025; Revised: March 05, 2026

Microcrystalline cellulose (MCC) is a powder-like multifunctional product with wide-spread and diverse applications. It is also a suitable raw material in the manufacture of microfibrillated cellulose. The commonly used MCC products have an average particle size of 40 - 60 μm. Products with a size of more than 100 μm are much more expensive, due to the difficulty in achieving the required degree of polymerization.

The results of this study show that for MCC production with a degree of polymerization less than 350 units, the hydrolysis temperature of the bleached hardwood pulp with dilute sulfuric acid should be 130˚C and higher. At a hydrolysis temperature of 120˚C and sulfuric acid content up to 2%, only modified cellulose is obtained. Under these conditions, the yield remains high with a minimum amount of dissolved xylose.

Keywords: mild acid hydrolysis, kinetics, degree of polymerization, microcrystalline cellulose

INTRODUCTION

Microcrystalline cellulose (MCC) is a multifunctional product with wide-spread and diverse applications (food, pharmaceutical and cosmetic industries). It is partially depolymerized cellulose which according to the European Pharmacopoeia has a degree of polymerization less than 350 [1, 2].

Microcrystalline cellulose is mainly produced from wood pulp and purified cotton linters. In industrial applications, only bleached dissolving pulp, obtained from raw materials such as softwood, hardwood, cotton, or straw, is utilized**.** The main advantage of dissolved pulp is its high purity while the disadvantage is its high price.

Toshkov *et al*. developed a method using 1% sulfuric acid solution as hydrolyzing medium and obtained a high yield, lowering the aggregation by optimization of the pulping process [3]. The classic process for MCC production, pioneered by Battista [4] is acid hydrolysis in a 2.5 normal solution of hydrochloric acid, followed by mechanical treatment. According to the Aalto Cell™ process, microcrystalline cellulose can be effectively produced from paper-grade pulp by sulfuric acid hydrolysis at a consistency of at least 8% and temperature of at least 80 °C, and the manufacturing process can be integrated into a kraft pulp mill [5].

A method for producing bleached microcrystalline cellulose from unbleached cellulose has also been developed, with the main advantage of efficient bleaching with significant saving of chemicals [6]. Our research group has been working for several years in the field of obtaining MCC from bleached paper-grade pulp. Technology has been developed for obtaining MCC by hydrolysis with dilute sulfuric acid in two stages, which allows the production of microcrystalline cellulose with high brightness, good particle uniformity and a desirable degree of polymerization, from hardwood bleached kraft pulp [7]. 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 xylan, and in the second hydrolysis stage - due to the removal of the absorbed humins.

The commonly used MCC products have an average particle size of 40-60 μm. The highest particle size of available MCC products is 250 μm. Products with a size of more than 100 μm are much more expensive, due to the difficulty in achieving the required degree of polymerization.

MCC is a suitable raw material in the manufacture of microfibrillated cellulose (MFC) as well [8, 9]. Considerable strength improvements have been gained by adding MFC to paper, composite structures, or other structures [10, 11]

Dilute acid hydrolysis of lignocellulosic materials and cellulose depends on temperature, time, and concentration, which is essential in optimizing microcrystalline cellulose production. At low acid concentrations and moderate temperature conditions, hydrolysis proceeds through a complex mechanism determined by the structural characteristics of the feedstock, including crystallinity, accessibility, and distribution of amorphous regions. Previous studies on dilute acid hydrolysis of hardwood and bleached pulp have

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shown that the process follows well-defined kinetic steps, reflecting the transition from rapidly hydrolyzed amorphous domains to more stable crystalline structures. In our previous studies, including those focused on the topochemical mechanisms of enzymatic and acid hydrolysis, we have highlighted the importance of the spatial distribution of reactive sites on the fiber surface and the influence of structural heterogeneity on the reaction kinetics. Our studies on dilute acid hydrolysis of bleached pulp for the production of microcrystalline cellulose and microfibrillated cellulose (MFC) confirm that temperature regimes, processing time and acid concentration strongly influence the reaction rate and the quality of the final product [12-14].

The aim of the present study is to investigate the temperature-time and concentration dependences of mild dilute acid hydrolysis of bleached pulp to microcrystalline cellulose and to modified pulp for microfibrillated cellulose.

EXPERIMENTAL

The experimental studies were carried out with bleached hardwood kraft pulp delivered by "Svilocel" AD, Bulgaria, which has been previously disintegrated and dehydrated.

The sulfuric acid hydrolysis was carried out in 1L stainless laboratory autoclaves at the following conditions: mass concentration of pulp 12.5%, charge with different acid percentages (1% and 1.5%), different temperatures (120°C and 130°C) and reaction times from 40 to 120 min. The process was stopped by cooling the autoclaves.

The obtained cellulose was washed and filtered through a filter with a pore size of 2 – 3 μm. The filtrate was analyzed by a Dionex HPLC system according to NREL Technical Report (NREL/TP-510-42623).

The degree of polymerization of cellulose was determined according to the SCAN-CM 15:88 standard, Mark-Hownik equation, and to the Japanese Pharmacopoeia standard used by JRS Pharma.

RESULTS AND DISCUSSION

The degree of polymerization (DP) is a main characteristic of microcrystalline cellulose (MCC). It is well known that DP decreases during the acid hydrolysis, which is basically associated with cellulose chain breakage. On the other hand, the extraction of the low-molecular xylan leads to a slight DP increase.

The kinetic studies of acid hydrolysis at temperatures of 120°C and 130°C and sulfuric acid charges of 1% and 1.5% show that in the time interval of 40 - 120 min, the degree of cellulose polymerization is in the range 295 – 611, as for DP lower than 350, temperature of 130° is required (Fig. 1).

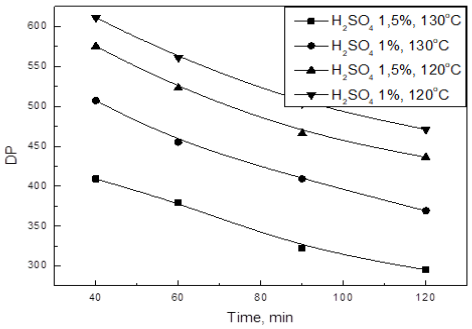

Figure 1. DP of MCC at different sulfuric acid charges *versus* temperature and time.

The degree of hydrolysis depends not only on temperature and time, but also on acid concentration. Under the experimental conditions, the yield of modified cellulose remains high [12]. The obtained results are presented in Table 1.

Table 1. Yields of modified cellulose at different temperatures and acid charges

Time, min	Yields of modified cellulose, %			
	T=120°C	T=120°C	T=130°C	T=130°C
	H_2SO_4 1%	H_2SO_4 1.5%	H_2SO_4 1%	H_2SO_4 1.5%
40	>99.0	>98.5	>98.5	>98.0
60	>98.5	>98.0	97.3	97.0
90	>98.0	97.3	96.7	96.5
120	>97.5	97.0	96.5	96.0

Dilute acid hydrolysis generates xylose during the process (Fig. 2). This could be related to the high pentosans content of the bleached pulp.

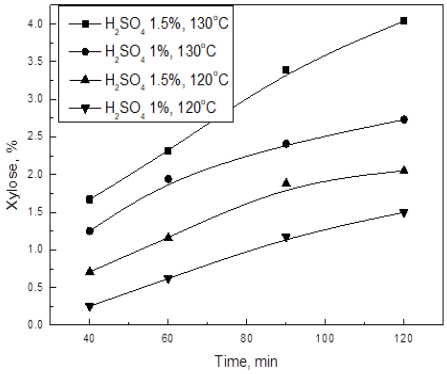

Figure 2. Xylose extraction at different temperatures and reaction times

As seen from Fig. 3, the yield of glucose increases much slower compared to that of xylose,

indicating that this parameter is not determining for the hydrolysis process.

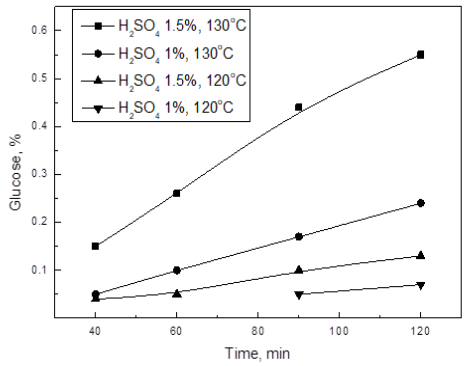

Figure 3. Glucose yield at different sulfuric acid charges, temperatures and time.

The kinetics of the process is investigated by the dimensionless quantity α which is determined as the relative change of DP and is calculated in correspondence with Equation (1):

$$\alpha = \frac{(1100-DP)}{1100} \quad (1)$$

where 1100 is the initial value of pulp DP.

Kinetic curves of the process of depolymerization are presented in Fig. 4.

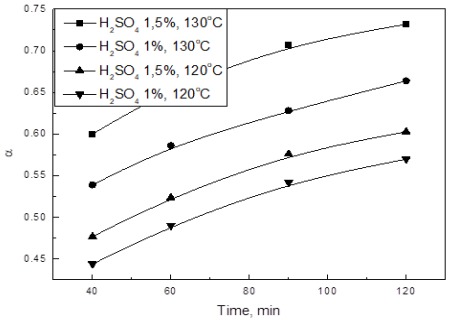

Figure 4. Kinetic curves of the hydrolysis process at different sulfuric acid charges and temperatures.

The applicability of different kinetic equations referring to different heterogeneous processes is verified (see Table 2). The kinetic investigation of the process of cellulose depolymerization shows that the modified Prout-Tompkins equation describes most precisely the heterogeneous process of dissolution of cellulose amorphous domains.

The modified Prout – Tompkins equation is used to describe the kinetics of solid decomposition of the fibrous structure of the pulp [13, 14]. The equation is presented in the following form:

$$\frac{\alpha}{(1-\alpha)} = (k.t)^{\chi} \quad (2)$$

where k is apparent rate constant, χ is power factor which takes values ($0<\chi<1$) characteristic for the system.

All kinetic curves are linearized in coordinates $ln\frac{\alpha}{(1-\alpha)}$ *vs.* lnt according to the logarithmic form of Equation (2).

$$ln\frac{\alpha}{1-\alpha} = \chi \ln k + \chi lnt \quad (3)$$

The dependences obtained are presented in Figure 5.

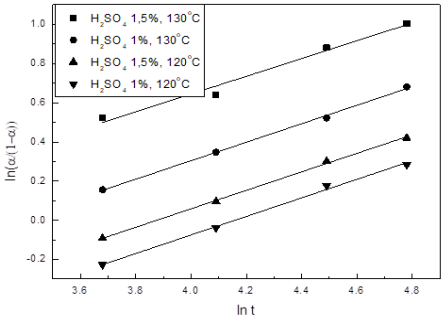

Figure 5. Linearization of Prout – Tompkins equation.

The value of the power coefficient χ is approximately equal to 0.47. The values of the apparent rate constant k are calculated and presented in Table 3.

Table 2. Comparison between correlation coefficient values obtained in the description of the process by different kinetic equations

Equation	R^2			
	120°C		130°C	
	H_2SO_4 -1%	H_2SO_4 -1.5%	H_2SO_4 -1%	H_2SO_4 -1.5%
Power kinetic equation $\ln(1-\alpha) = -kt$	0.99344	0.98758	0.99443	0.98224
Exponential kinetic equation $\alpha = k + a^{-1}.lnt$	0.99665	0.99254	0.99882	0.9903
Modified Prout – Tompkins equation $\frac{\alpha}{(1-\alpha)} = (k.t)^{\chi}$	0.99471	0.99809	0.99767	0.99136

Table 3. Values of the apparent rate constant k

Experimental conditions	Rate constant $k \times 10^{-2}$, min^{-1}
H_2SO_4 1.5%, 130°C	8.3
H_2SO_4 1%, 130°C	3.4
H_2SO_4 1.5%, 120°C	2.0
H_2SO_4 1%, 120°C	1.5

As can be seen from Table 3, the highest value of the rate constant is obtained at acid concentration of 1.5% and temperature of 130˚C, which affects the yield of MCC.

CONCLUSIONS

The degree of hydrolysis depolymerization of bleached hardwood pulp depends not only on temperature and time, but also on sulfuric acid concentration.

Under the studied conditions, the amounts of dissolved substances remain minimal while the yield of modified cellulose remains high.

The kinetic investigation of dilute sulfuric acid hydrolysis of bleached hardwood kraft pulp aiming microcrystalline cellulose production shows that the modified topochemical Prout – Tompkins equation describes the process of the pulp depolymerization. The temperature – time dependence obtained can be used for control and simulation of the process of depolymerization of pulp to microcrystalline cellulose.

Acknowledgement: *This research is supported by the Bulgarian Ministry of Education and Science under the National Program "Young Scientists and Postdoctoral Students-2".*

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