



Investigation of reaction activity of cellulose and its products of acid hydrolysis

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ABSTRACT

A comparative study of the reaction activity of cellulose and its acid hydrolysis products (microcrystalline and nanocellulose) during periodate oxidation and carboxymethylation were provided.

The functional composition of the cellulose, microcrystalline cellulose and nanocellulose was investigated and determined the number of formed functional groups in the hydrolysis products.

It was found, that with increasing reaction activities among cellulose-microcrystalline cellulose-nanocellulose, depend on quantity of formed functional groups and their high surface area in the same sequences.

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KEYWORDS

Cellulose;
Microcrystalline cellulose;
Nanocellulose;
Oxidation;
Carboxymethylation.

INTRODUCTION

Reaction activity of celluloses and its derivatives in heterogeneous processes is defined, first of all, by the content and nature of functional groups, and also their surface area.

From this point of view cellulose could be consider as polymeric polyatomic spirit, in elementary unit of macromolecule which contained three hydroxyl groups.

Exactly individual properties of hydroxyl groups let to carry out as a result of their chemical transformations synthesis of simple and multiple ethers of cellulose^[1].

Possibility of regulation of their properties and expansion of area of their application^[2,3,4] appears introduction of additional functional groups in cel-

lulose structure.

The aim of present work is carry out of comparative investigation of reaction activity of cellulose and its products of acid hydrolysis (microcrystalline cellulose and nanocellulose) during periodate oxidation and carboxymethylation.

EXPERIMENTAL

The research objects were the cotton cellulose (CC), microcrystalline cellulose (MCC), nanocellulose (NC) and their functionalized derivatives.

MCC and NC obtained according to^[6]. Particle size of celluloses were determined by AFM and EM methods. For the oxidation of the samples used 2-5% aqueous solutions of iodic acid, oxidation unit

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is 1:5-1:10, the oxidation temperature is 22-25°C. Carboxymethylation of cellulose samples performed by pretreatment with alkaline solution followed by etherification of the sodium salt of monochloroacetic acid.

Functional groups of the samples was determined by the method^[5]. The content of sulfonic groups was determined by chemical analysis.

The kinetics of the oxidation reaction was determined by potentiometric titration by measuring the amount of flow of oxidant -periodic acid - HJO_4 and produced iodic acid - HJO_3 .

RESULTS AND DISCUSSION

At processes of acid hydrolysis of cellulose occur oxidation - hydrolytic proceed, bring to decrease of the size particles, degree polymerization and to formation of new functional groups, first of all, aldehydic and carboxylic groups.

Investigation of determination of functional groups in CC, MCC and NC were conducted.

As is shown in TABLE 1, increasing concentra-

tion of the hydrolyzing agent (sulfuric acid) with simultaneous decreasing the size of particles to occur an increase the content of end of aldehyde groups. changing carboxylic groups could be explained oxidation the part of end aldehydic groups till carboxylic groups.

The increasing content of functional groups of cellulose at hard conditions of hydrolysis, it could be explained also increase to speed of the oxidising processes proceeding in cellulose.

The functional groups, formed after hydrolysis, increased reaction activity of celluloses that permit to carry reactions of oxidation, etherification and etc. by softer conditions.

Moreover the possibility of behavior reaction etherification cellulose, with formation sulfo cellulose weren't except:

It was found that with increasing the concentration of hydrolyzing agent, the size of particles of hydrolyzed cellulose decreased but content of sulphur increased (TABLE 2) that confirmed particulate etherification of cellulose at process its hydrolysis. This data accordance with results of works^[7].

TABLE 1 : The content of functional (aldehyde and carboxyl) groups in the samples which were obtained at the different concentration of hydrolyzing agent

Nº	Samples	Concentrations of sulfuric acid, %	Average size of particles	Content of COH, %	Content of COOH, %
1	CC	-	-	0.040	0.024
2	MCC	10	400 µm	0.053	0.028
3	MCC	20	100 µm	0.081	0.029
4	MCC	40	20 µm	0.093	0.031
5	NC	61	400 nm	0.108	0.035
6	NC	66	290 nm	0.267	0.039

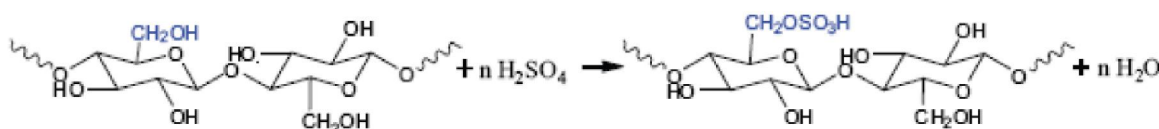


TABLE 2 : Influence of concentration of hydrolyzing agent to content sulphur group (on sulphur) in hydrolysis products

Samples	Concentrations of sulfuric acid, %	Content of sulphur	Average of size particles
1	10	0.05	400 µm
2	20	0.09	100 µm
3	40	0.28	20 µm
4	61	0.62	400 nm
5	66	1.35	290 nm

At periodate oxidation of cellulose it irreversible it is break down glucopyranosic cycle between atoms C_2 and C_3 with formation dialdehyde link^[8].

The speed and degree of oxidation of cellulose is defined by structure of cellulose and oxidation conditions.

The kinetic reactions of oxidation CC, MCC and NC at expense of HJO_4 and influence of pH- medium at initial stages were studied.

For the carrying out of reaction oxidation of cellulose by an ions periodate (IO_4^-) till dialdehyde - cellulose theoretically on each mole cellulose links it is required 0,1 mole an ion IO_4^- thus degree of polymerization stay unchangeable^[9].

The mechanism of periodate could be concluded to sorbtion of oxidizer of cellulose with formation of multiple aether in type single-loading anion (I) which easy dehydrate in anion (II), with the next oxidation of cellulose, bring to decomposition of structure (II) to final product of reaction (III) slowly and monomolecularic, on electronic mechanism similar to process, taking place at intramolecular transformations^[10] and quantity of an oxidizer absorbed from solution transfer to proportionally on quantity of the oxidised cellulose links at final product^[11].

Experimental studies of selective oxidation of cellulose, MCC and NC IO_4^- ions showed that the amount of aldehyde groups is always less than the amount absorbed HC, MC and SC of ions IO_4^- . This discrepancy increases in the number of NC-HC-MCC, and it is explained by a low rate of decomposition structures II to III on the structure of monomolecular mechanism by intramolecular transformations.

Kinetic curve absorption of ions IO_4^- from solution of oxidizer CC, MCC and NC (Figure 1) have shown that at 22 °C speed of formation of complexes I and II at initial stages is enough big in that case of NC and MCC, and sorption an oxidizer at 2 hours make up 80 % and 70 % respectively.

Difference from them, the CC forms complexes I and II only after 8 hours of processing by iodic acid that could be explained specificity its morphological and supramolecular structures.

At oxidation of cellulose by ions IO_4^- formed ions IO_3^- iodine acids characterise formation of structure III and regarding, with respect to quantity of ions IO_3^- can be calculate of quantity formed dialdehydic links.

Speed of formation iodine acids (Figure 2) sig-

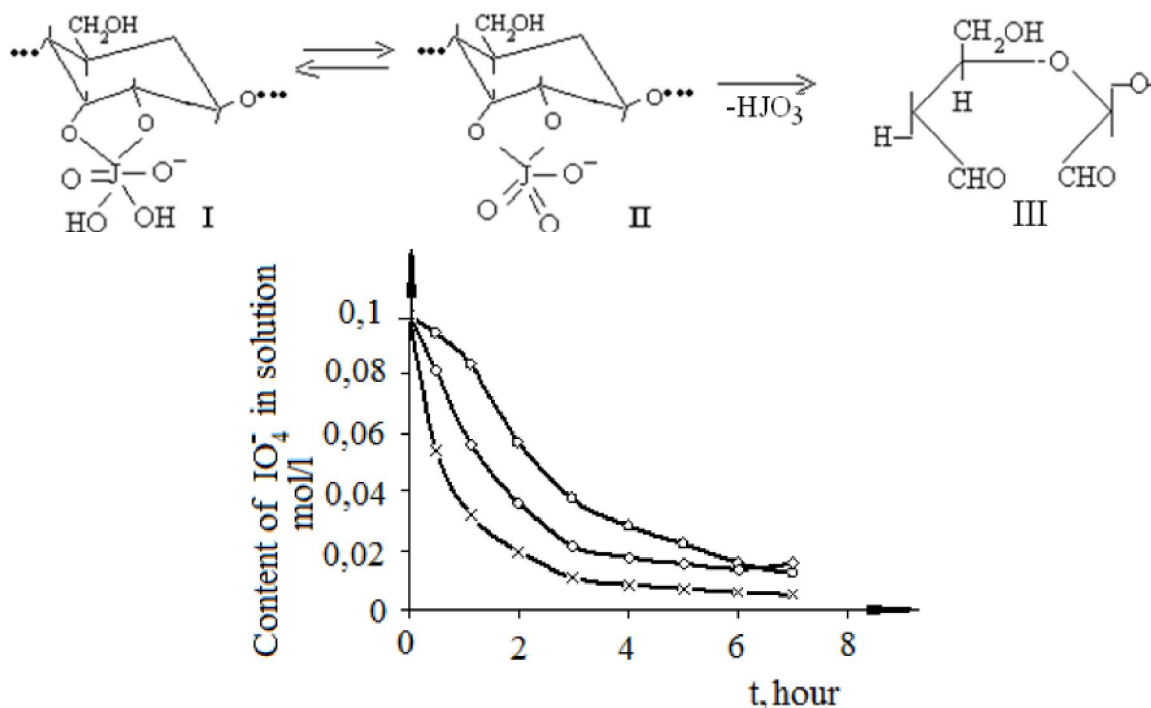


Figure 1 : Dependence of content of ions IO_4^- (iodic acid) in solution from time at oxidation CC (-o-), MCC (-◇-) and NC (-x-)

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nificantly slowly, than speed of absorption of iodic acid (Figure 1).

It is established that speed of decomposition of structure II to structure III increases at line CC-MCC-NC that is connected with increase their superficial area in the CC-MCC-NC.

The calculating area of NC surface 1000 times more than, that the same quantity of MCC samples.

Moreover, the content of functional groups of CC, MCC and NC (TABLE 1 and 2) also influence on oxidation rate.

These factors have been studied in^[12], where it was revealed that samples prepared by acid hydrolysis of cellulose has a considerably high oxidation rate compared to the original cellulose mobility due primary hydroxyl groups and the apparent activation energy of the oxidation reaction MCC approaching activation energy of oxidation of esters in solution.

Influence studying of ph on oxidation process

has shown that the oxidation mechanism is identical to oxidation α - glycols in homogeneous environment and differs only in speed of process and differs only by the speed and heterogeneous processes.

Under certain pH range of a single charge (I) can be dehydrated to form a structure of type (II), by e-rearrangement.

It was found that, the speed of oxidation passes through wide maximum in an interval pH=3-7 where prevail single-charge complexes (I) (Figure 3).

In more acid and alkaline scale where prevail uncharged complex IV and doubly charged of complex V, speed of reaction strongly decreases^[12] and these complexes cannot decompose so simply, as structure I.

Investigated determination of time of limiting oxidation of samples CC, MCC and NC (TABLE 3) and it is found that speed of overall value periodate oxidation of NC the 8-10 times high, than CC, which inversely proportional time of limiting oxidation.

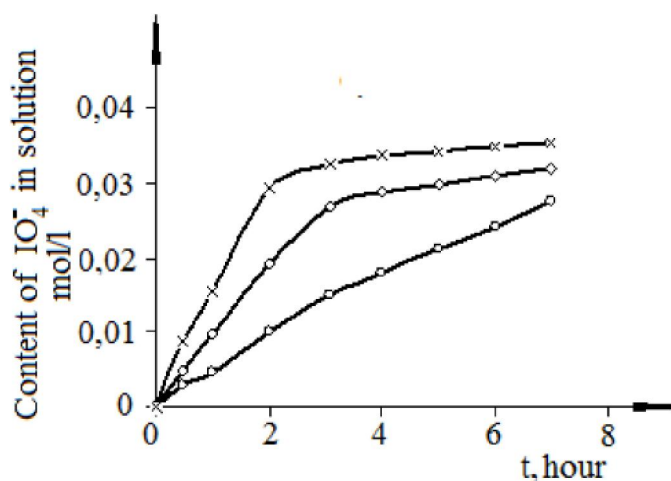


Figure 2 : Kinetic curve formations of ions IO_3^- (iodic acids) at oxidation CC (-o-), MCC (-o-) and NC (-x-)

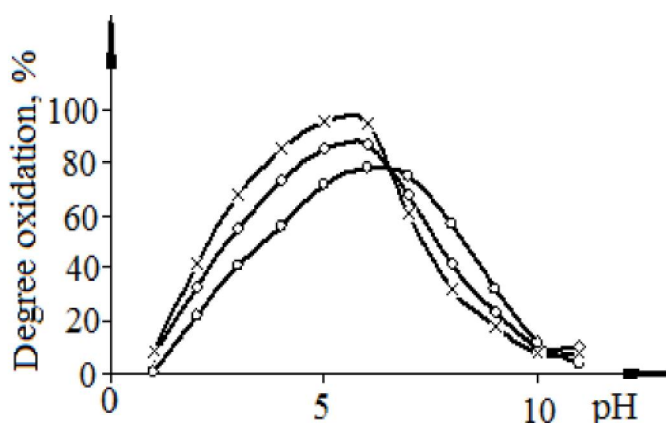


Figure 3 : Influence pH to degree of oxidation CC (-o-), MCC (-o-) and NC (-x-)

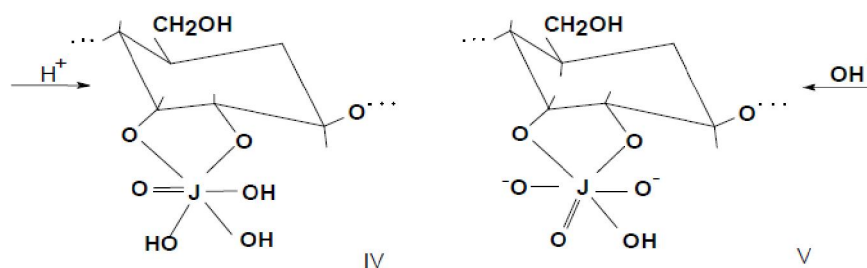


TABLE 3 : Degree and time of oxidation of CC, MCC and NC samples

Samples	Average size of particles	Time of oxidation, hour	Degree of oxidation	
			By number of iodine	By hydroxyl amine
Cellulose	-	24	0.94	0.98
MCC	250 μm	5	0.96	0.99
NC	400 nm	2	0.95	0.98

TABLE 4 : Comparative characteristics of the carboxymethyl cellulose (CMC) samples

Quality indicators	CMC from CC	CMC from MCC	CMC from NC
Degree of substitution	0,35	0,38	0,52
Degree of polymerization	870	160	100
Base substance content, %	52	53	51
Water solubility, %	23,1	96,6	99,7
pH of 1% aqueous solution	11,0	9,0	9,2

It was established experimentally that the MCC samples exposed quantitatively periodate oxidation for 5-8 hours at 22-25°C and NC samples oxidized for 0.5-1 hours.

Experimentally established that the samples of MCC practically quantitatively examine periodate to oxidation for 5-8 hours at 22-25 °C, but samples NC subjected to oxidation for 0.5-1 hours.

It is shown that the products of MCC oxidation are as a hydrogel, and the samples of NC are as a solution near to a true solution.

They could be separate by the method of sedimentation in acetone, which was freed from surplus of an oxidizer by washing with acetone.

The high reactivity of nanocellulose compared with microcrystalline cellulose and cotton also observed in the reactions of their heterogeneous carboxymethylation, since the reaction rate is determined by the number of interacting components of effective collisions per unit time.

Comparative studies have shown that under the same conditions, the quality of the carboxymethylation of the carboxymethylated cellulose samples have a linear dependence on the na-

ture of the feedstock. The degree of substitution ($0,35 < 0,47 < 0,53$) and the solubility in water ($23,1 < 83,6 < 99,7$) increases with a transition from macro to micro and nanosized cellulose particles (TABLE 4).

Increasing the reaction activity of the acid hydrolysis of cellulose in the carboxymethylation reaction is related to the increase and decrease in dimension of the surface area of cellulose particles creating availability etherifying agents^[13]. Moreover, the use of ultrasonic dispersion and the microwave irradiation in the preparation of NC also enhances the reactivity due to the splitting of the particles of micro and macro cracks that were identified by microscopic studies^[14]. Smaller particles, while maintaining the DP, and microwave irradiation microcracks on the surface of the MCC particles which upon swelling also increases the reactivity of NC by increasing the possibility of contact with the surface of the alkylating agent.

The effect of DP and DS to solubility of carboxymethyl cellulose was showed that the increase DS and decrease of DP improves their solubility in water while reducing a gel-fraction.

TABLE 5 : Influence of Na-CMC DS and DP on the solubility in water

Samples for carboxymethylation	DS of Na-CMC	DP of Na-CMC	Water solubility,%	Contents of the gel fraction,%
CC	0,85	670	98,9	0,7
	0,65	740	97,8	2,0
	0,45	840	42,9	24,6
	0,35	870	23,1	41,3
	0,65	180	100	-
MCC	0,56	250	100	-
	0,48	160	100	-
	0,38	160	98,0	0,7
	0,30	190	82,0	1,8
	0,52	100	100	-
	0,42	110	100	-
NC	0,33	120	100	-
	0,24	120	100	-
	0,15	125	99,7	-

Boundary complete solubility of CMC samples obtained from CC is an average at DS = 0.85, for MCC at DS= 0.38 and for NC at DS= 0.15 (TABLE 5).

Despite the high crystallinity of MCC and NC based on the data on defect of crystallite and lightness of decay of MCC and NC in liquid media under microwave irradiation prior to smaller structural fragments of these drugs will exhibit a high reactivity with various chemical actions.

Studies have shown the possibility of obtaining of low viscosity Na-CMC samples, highly soluble in water at low values of DS 0,15 ÷ 0,20.

Obtained low-viscosity samples are great interest for using in the medical, pharmaceutical and food industries.

CONCLUSIONS

Thus, the functional composition of cellulose and its products of acid hydrolysis investigated and it is revealed that the changes in the conditions of hydrolysis proceeds simultaneously change both in particle size and the number of functional groups.

Comparative study of the regularities were conducted and optimal conditions periodate oxidation and carboxymethylation of CC, MCC and NC were found.

It was shown, that with increasing reaction ac-

tivities among cellulose-microcrystalline cellulose-nanocellulose since carboxymethylation, at the expense of decreasing the DP and increasing the total surface area and increasing the content of carbonyl and carboxyl end groups in this condition that increase the number of effective collisions oxidant molecules with glycol groups in glucopyranose rings.

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