

## OBTAINING MICROCRYSTALLINE CELLULOSE FROM SOFTWOOD AND HARDWOOD PULP

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Conditions for obtaining microcrystalline cellulose (MCC) by the thermocatalytic method from hardwood (birch, aspen) and softwood (pine) bleached sulphate pulp have been developed. After thermocatalytic treatment, cellulose polymerization degree has decreased to the so-called levelling-off degree of polymerization (LODP), which, in the case of birch, aspen and pine wood pulp, made up 450, 370 and 250 units, respectively. After grinding the destructed pulp in a ball mill, MCC powder samples were obtained with particles, the major part of which had sizes of 2-20  $\mu\text{m}$ . In terms of physico-chemical indices investigated in this work, the obtained samples conform to the pharmacopoeia requirements. Dispersing the destructed pulp in water medium, at a sufficiently high cellulose concentration ( $\geq 8\%$ ), MCC gel samples were prepared, with rheological properties typical for liquid crystalline polymers. The indices of the obtained hardwood and softwood MCC were compared.

*Keywords:* Microcrystalline cellulose, Thermocatalytic destruction, Viscosity, Shear rate, Hardwood, Softwood

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### INTRODUCTION

At present, microcrystalline cellulose (MCC) is used in various fields such as pharmacy, cosmetics, the food industry, the plastics processing industry, etc. (see, for example, Ioelovich and Leykin 2004).

In the powder form, it is used, for example, as a filler and binder in medical tablets and food tablets for dietary purposes. In the gel form, MCC is used as a viscosity regulator, a suspending agent, emulsifier in different pastes, creams, etc.

In our earlier work, a thermocatalytic method for obtaining MCC has been developed (Laka and Chernyavskaya 1996).

In the present work, optimal thermocatalytic treatment conditions were developed for obtaining MCC from softwood and hardwood pulp, and the properties of the obtained MCC samples were investigated.

### EXPERIMENTAL

#### Development of Thermocatalytic Treatment Conditions

Hardwood (birch and aspen) and softwood (pine) bleached sulphate pulp samples were used for the thermocatalytic treatment (Laka et al. 2000). Pulp samples were impregnated with acid catalyst (e.g., hydrochloric acid) solutions of different concentrations and dried during 5-6 hours until the moisture content in the sample

reached 3%. The dependence of the degree of polymerization of cellulose samples, which was determined from the intrinsic viscosity of cellulose cadoxen solution (Obolenskaya et al. 1991), on the hydrochloric acid concentration and thermal treatment temperature was determined. Optimal thermocatalytic treatment conditions, at which the degree of polymerization reaches its constant value, were established.

### **Obtaining of MCC Powders and Gels**

To obtain MCC powders, the degraded pulp samples were ground in a ball mill. After grinding, they were washed-off from the remaining acid, dried at 80°C and additionally ground to get rid of agglomerates.

To prepare MCC gels, the degraded cellulose pulp samples were dispersed in an aqueous medium in a ball mill. At sufficiently high cellulose concentrations ( $\geq 8\%$ ), MCC gel samples were obtained.

### **Investigation of the Properties of the Prepared MCC Powder and Gel Samples**

The structural and physico-chemical properties of the obtained MCC and the rheological properties of the gels were investigated.

For studies of the form and sizes of powder particles, an optical microscope BIOLAM and a scanning electron microscope Tescan 5136 were used.

The sizes of the particles present in the gels were investigated by the photon correlation spectroscopy method on a Zetamaster S 500 ZEM. For measurements, the fine fraction of MCC gels was used, which was obtained by way of precipitation of very diluted gels and removal of precipitated particles. This was necessary to avoid sedimentation during the measurements, undesirable when using the given method.

Water retention value (WRV) was determined by the Jayme method (Jayme and Hahn 1960).

Physico-chemical properties, for example, solubility, pH value, mass losses when drying etc. were determined by the methods specified in the European Pharmacopoeia, 5<sup>th</sup> Ed. (2005).

The rheological properties of the gels were determined using a viscosimeter Rheotest-2 with coaxial cylinders in the shear rate range from 0.50 to 437 s<sup>-1</sup> at 20°C.

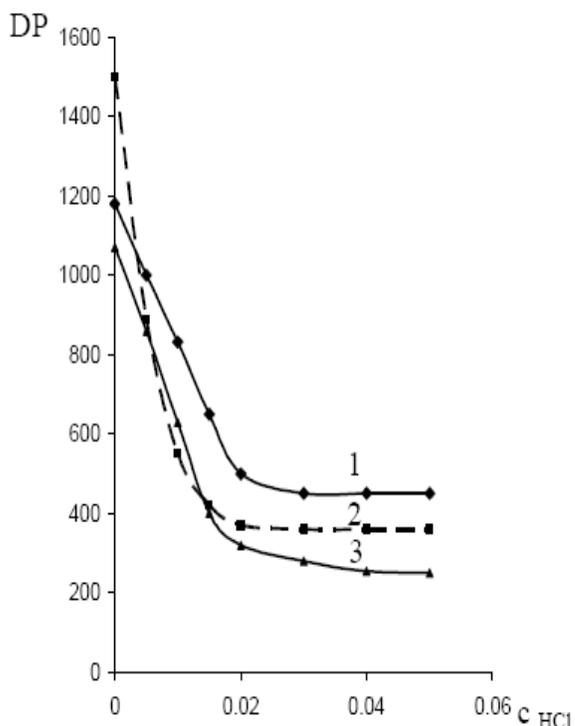
## **RESULTS AND DISCUSSION**

### **Change in Degree of Polymerization of Cellulose after Thermocatalytic Treatment**

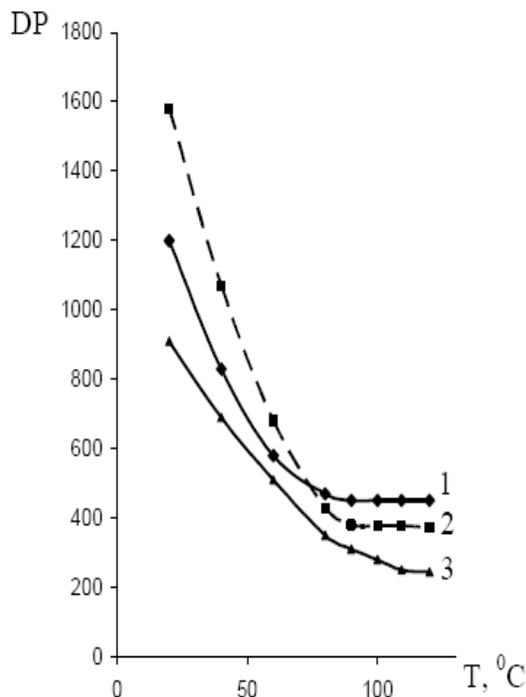
Figure 1 shows the dependence of the change in the degree of polymerization of hardwood and softwood cellulose on the hydrochloric acid solution concentration at the thermal treatment temperature 110°C. As can be seen, with increasing hydrochloric solution concentration, the degree of polymerization first decreases dramatically, while, at a 0.025% concentration, in the case of hardwood and at a 0.04% concentration in the case of softwood, reaches a constant value – levelling-off degree of polymerization (LODP), when the amorphous part is destructed, while the crystalline one remains almost intact.

Figure 2 shows the dependence of the degree of polymerization of hardwood and softwood cellulose on the thermal treatment temperature at a constant hydrochloric acid

solution concentration (0.04%). With increasing thermal treatment temperature, LODP is reached at 90°C and 110°C for hardwood and softwood cellulose, respectively.



**Fig. 1.** Cellulose polymerization degree versus hydrochloric acid solution concentration at the treatment temperature 110°C for birch (1), aspen (2) and pine (3) pulp samples



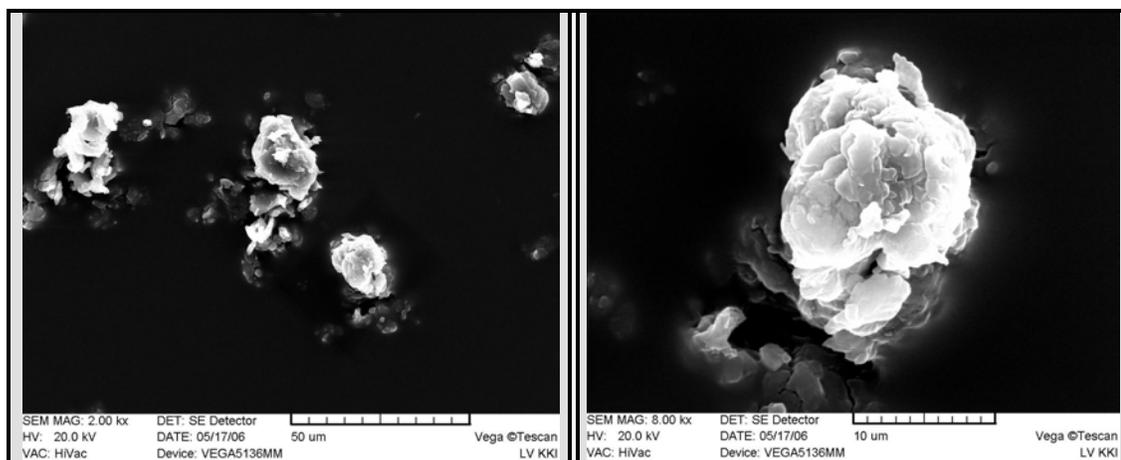
**Fig. 2.** Cellulose polymerization degree versus thermal treatment temperature at the hydrochloric acid solution concentration 0.04% for birch (1), aspen (2) and pine (3) pulp samples

From the obtained results, the following thermocatalytic treatment conditions for reaching LODP were established: hydrochloric acid solution concentration 0.025-0.05% and 0.04-0.10%; thermal treatment temperature 90-120°C and 110-130°C for hardwood and softwood, respectively.

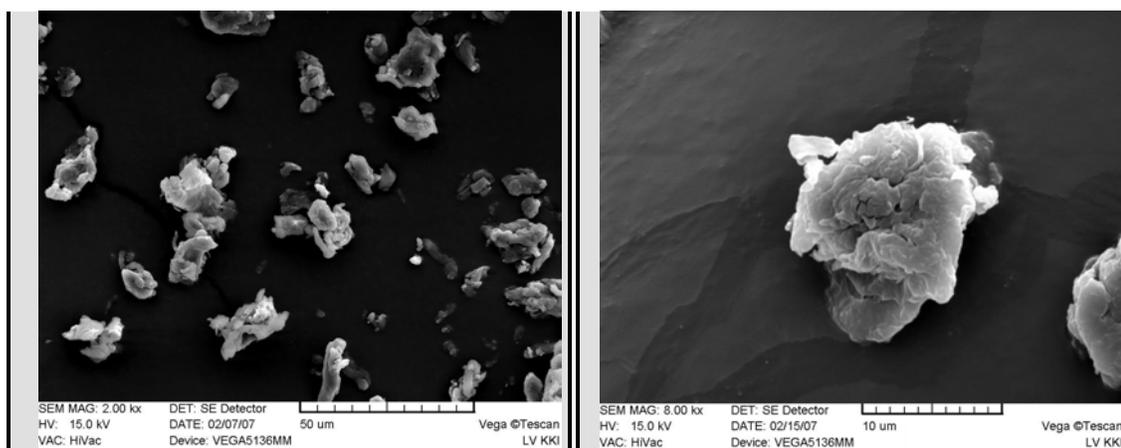
### Properties of Hardwood and Softwood MCC Powders

After grinding in a ball mill the pulp sample destructed to LODP, MCC powder samples were obtained, whose particles' longitudinal and transversal sizes differed little. The longitudinal size of 60% of particles and the transversal size of 80% of particles are in the range 2-20  $\mu\text{m}$ . The maximum particle size for hardwood and softwood MCC powder does not exceed 60 and 100  $\mu\text{m}$ , respectively.

Figures 3a and 3b shows micrographs of aspen and pine powder particles obtained using a scanning microscope at two different magnifications.



**Fig. 3a.** Electron micrographs of aspen MCC powder particles



**Fig. 3b.** Electron micrographs of pine MCC powder particles

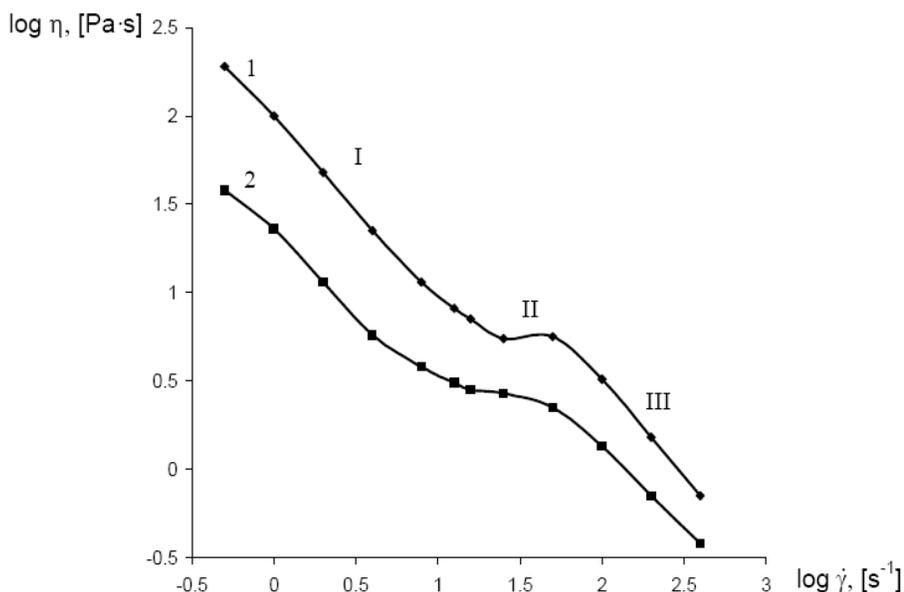
**Table 1.** Physico-chemical and Quality Indices of Hardwood and Softwood MCC and Pharmacopoeia Requirements

No.	Index	Hardwood MCC	Softwood MCC	Requirements of the Pharmacopoeia
1	Solubility	Corresponds	Corresponds	Practically insoluble in water, 96% ethanol, diluted acids, acetone, toluene
2	pH	6.1-6.5	6.2-6.8	5.5-7.0
3	Weight losses upon drying	5.1-5.9	3.7-5.8	No more than 6
4	Water-soluble substances, %	0.28-0.31	0.12-0.16	No more than 0.2
5	Starch and dextrans	Corresponds	Corresponds	0.1 of the preparation in 5 ml of water. 0.2 ml of 0.05 M iodine solution is added. Blue and red-brown colours must not appear
6	WRV, %	72-85	50-55	-

Table 1 shows quality indices for hardwood and softwood MCC samples. In terms of physico-chemical indices, they conform to pharmacopoeia requirements, although the chemical purity of the obtained hardwood MCC samples is somewhat lower, which can be explained by the fact that they are not additionally bleached. WRV for hardwood MCC powders is by 30% higher than for softwood.

### Properties of Hardwood and Softwood MCC Gels

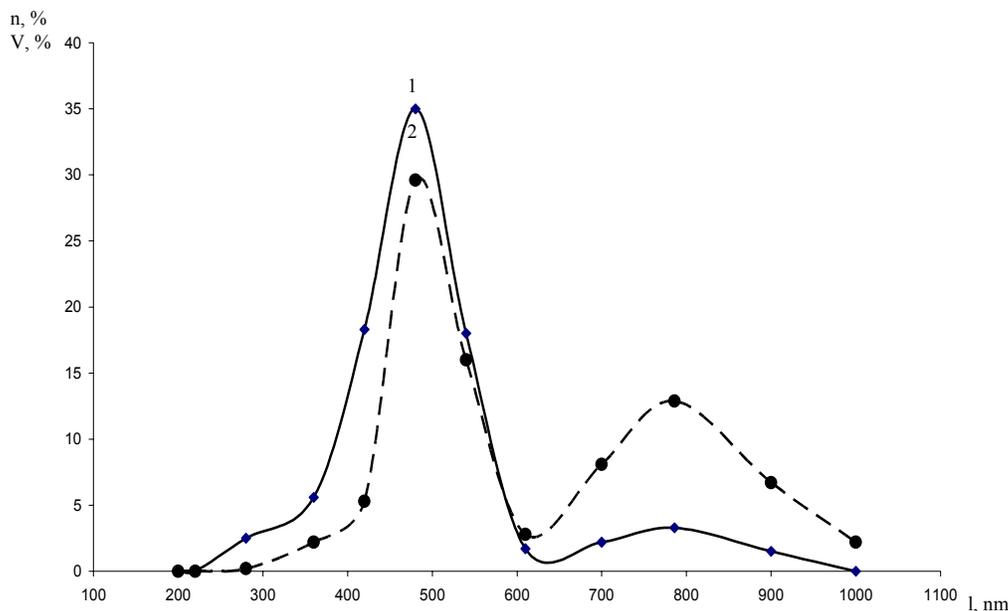
Figure 4 shows flow curves for the obtained hardwood and softwood MCC gel samples. As can be seen, at the same cellulose concentration (10%), viscosity in the whole shear rate range in the case of hardwood MCC gel is higher. The flow curves for both hardwood and softwood MCC gels have three pronounced regions, which, as has been shown in our earlier works (for example, Laka et al. 2003), is connected with their liquid crystalline structure. Region I corresponds to the gel flow with microcrystallite domains aligned in different directions, region II corresponds to the domains' break-up and the microcrystallites' alignment in the flow direction, and region III corresponds to the gel flow with microcrystallites aligned in the flow direction.



**Fig. 4.** Viscosity versus shear rate for birch (1) and pine (2) MCC gels

The liquid crystalline structure formed by microcrystallites is validated also by the distribution graphs of the gel fine fraction particle number and their occupied volume in their longitudinal size, determined by the photon correlation spectroscopy method (Fig. 5).

It can be seen that the maximum of the distribution graphs is located at 500 nm, which is close to the microcrystallite longitudinal sizes. The transversal sizes are 30-100 times smaller. Thus, by dispersing the destructed pulp in water medium, attrition of the microcrystallites occurs. The presence of microcrystallite whiskers in dispersions at their sufficiently high concentration provides an MCC gel formation with liquid crystalline rheological properties.



**Fig. 5.** Percentage distribution graphs of the number of particles  $n$  (1) and the particle-occupied volume  $V$  (2) for the fine fraction of the MCC gel with respect to the longitudinal size of particles

## CONCLUSIONS

1. In this work, the thermocatalytic treatment conditions were established for degradation the hardwood and softwood pulp till the levelling-off degree of polymerization, which, in the case of birch, aspen and pine, were 450, 370 and 250 units, respectively.
2. After grinding in a ball mill the degraded pulp, MCC powder samples were obtained. The major part of the powder particles had the sizes 2-20  $\mu\text{m}$ . The investigated physico-chemical indices of the obtained MCC powder samples conform to the European Pharmacopoeia requirements.
3. After dispersing the degraded pulp in aqueous medium, MCC gel samples were obtained, with rheological properties typical for liquid crystalline polymers.

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