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Research article

Synthesis of Methylcellulose from Industrial Hemp: Optimization of Mercerization and Methylation Conditions with Dimethyl Sulfate

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Abstract

Methylcellulose (MC) is widely used in various industries, including construction, pharmaceuticals, and biomedicine. The aim of this work was to develop a laboratory method for the synthesis of MC from cellulose obtained from industrial hemp – a renewable and economical raw material. Cellulose was isolated by two methods: organosolv (method A) and sodium hydroxide-ammonia (method B). MC synthesis was carried out in a heterogeneous medium (toluene–isopropanol mixture) using dimethyl sulfate as a methylating agent. The effects of NaOH concentration during mercerization (20-50 %) and the molar ratio of cellulose to dimethyl sulfate (from 1:1.28 to 1:3) on the degree of substitution (DS) and water solubility of the product were studied. The obtained samples were characterized by IR spectroscopy, ^{1}H and ^{13}C NMR, as well as gas-liquid chromatography (GLC) after cleavage with in situ generated hydroiodic acid. An increase in the amount of dimethyl sulfate was shown to regularly increase DS and the yield of the water-soluble fraction. A non-monotonic dependence of DS on alkali concentration was found, i.e. minimum values were observed at 20 and 30 % NaOH, while the maximum was at 50% NaOH. The highest degree of substitution (DS = 1.38-1.70) and methoxy group content (23.6-28.4 %) were achieved using organosolv cellulose, mercerization with 50 % NaOH, and a cellulose : dimethyl sulfate molar ratio of 1:2.5-3.0. A convenient GLC method for the determination of methoxy groups was developed, giving results that correlated well with NMR data. The obtained results allow us to recommend industrial hemp as a promising raw material for the synthesis of water-soluble cellulose ethers.

Keywords: methylcellulose; industrial hemp; synthesis; dimethyl sulfate; degree of substitution; FTIR spectroscopy; ^{1}H and ^{13}C NMR spectroscopy; GLC method

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1. Introduction

In the modern world, the transition to a «green» economy makes the use of renewable plant raw materials particularly important (Jatoi et al., 2023; Ntunka et al., 2025). Cellulose is the most abundant biopolymer in nature and is well-suited for creating new materials. Cellulose is available, safe for living organisms, biodegradable, and readily undergoes chemical reactions (Madhushree et al., 2024). However, the direct use of pure cellulose is difficult due to its poor solubility in common solvents caused by strong intra- and intermolecular hydrogen bonds. An effective way to overcome this limitation is the chemical modification of cellulose to obtain its soluble derivatives, such as cellulose ethers (Tufan & Özel, 2024; He et al., 2025). Among them, methylcellulose (MC) occupies a special place, combining good water solubility, adjustable viscosity, high water retention, and thermal gelation reversibility (Ergun & Huebner-Keese, 2016). In recent years, special interest has been focused on the use of methylcellulose for the preparation of thermosensitive hydrogels and bioinks for 3D bioprinting, which opens broad prospects for its application as a “smart” biomaterial in tissue engineering (Ahlfeld et al., 2020; Bonetti et al., 2021; Xiong et al., 2024). Because of this, MC is widely used in the construction industry (Majewicz et al., 2002), pharmaceuticals (Garg et al., 2025), and in the food industry (Elfawal et al., 2025).

The traditional raw materials for producing cellulose ethers are wood pulp or cotton linter (Majewicz et al., 2002). However, the search for alternative, rapidly renewable and underutilized sources is of great scientific and practical interest. In this aspect, hemp fibre obtained from the bast part of the stem of specially bred non-psychoactive varieties of hemp (*Cannabis sativa* L.) is a promising raw material. Industrial hemp is a highly productive agricultural crop whose stems contain a significant amount of cellulose with a high degree of polymerization. This makes the use of hemp cellulose an economically viable and renewable alternative to cotton or wood cellulose for the synthesis of cellulose ethers, in particular methylcellulose.

The classical industrial synthesis of MC involves the alkylation of alkali cellulose with chloromethane under pressure in autoclaves, a process that requires specialized and expensive equipment (Grover, 1993). For laboratory screening, however, it is more convenient to use alternative methylating reagents that do not require autoclaving. One such reagent is dimethyl sulfate. Despite its high toxicity, it is widely used in laboratory practice due to its good solubility in organic solvents, high reactivity, and suitability for reactions at atmospheric pressure. The successful use of dimethyl sulfate for the methylation of cellulose from various sources has been described: sugar cane bagasse (Viera et al., 2007), mango seed fibres (Vieira et al., 2012), wheat straw (Kumar & Walia, 2017), snake fruit (*Salacca zalacca*) (Wahyuningtyas et al., 2021), waste newspaper (Oliveira et al., 2010), bacterial cellulose (Oliveira et al., 2015), and corn cobs (Singh, 2013), as well as wheat and barley straw and rice husks (Biswas et al., 2013). However, no such systematic studies have been performed for cellulose from industrial hemp.

The aim of this work was to develop and optimize a laboratory method for the synthesis of methylcellulose from cellulose isolated from industrial hemp stems using dimethyl sulfate as a methylating agent.

To achieve this goal, the following tasks were set: isolate cellulose from hemp by two methods (organosolv and sodium hydroxide-ammonia) and evaluate its degree of polymerization; study the effect of NaOH concentration and treatment time on cellulose degradation during mercerization; carry out methylation of mercerized cellulose at varying molar ratios of cellulose to dimethyl sulfate and alkali concentration; characterize the

obtained methylcellulose samples by degree of substitution (using ^{1}H and ^{13}C NMR, as well as GLC after treatment with hydroiodic acid) and determine their water solubility to establish a relationship between synthesis conditions and product properties.

The success criteria for the synthesis were: achieving a degree of substitution ≥ 1.3 (which ensures water solubility) and obtaining a clear or slightly opalescent 2% aqueous solution.

2. Materials and Methods

2.1 Materials

Hemp samples (industrial hemp) containing cellulose were provided by LLC «Mordovskie Penkozavody» (Insar, Republic of Mordovia). Dimethyl sulfate, sodium hydroxide, isopropanol, acetic acid and ethylenediamine were purchased from Vekton (St. Petersburg, Russia). All chemical reagents in this study were used as supplied by the manufacturers without any additional purification. Deuterated water (D_2O) was purchased from Solvex LLC (99.8 atom % deuterium).

Coarsely ground hemp fibers were dried in an oven at 100-105°C for 6 h. Then, to remove lignin and hemicellulose, they were subjected to two types of treatment: organosolv or sodium hydroxide-ammonia. After that, they were dried and re-ground to a fraction of 0.1-0.3 mm using a «Farmer» grain crusher (UralSpetsMash, Miass, Russia).

2.2 Methods

IR spectra of samples pressed into tablets without KBr were recorded using an attenuated total reflection (ATR) attachment (ZnSe crystal) on an InfraLUM FT-08 FTIR spectrometer in the range 400-4000 cm^{-1} with a resolution of 4 cm^{-1}, using Bessel apodization, with a scan time of 60 s and 93 scans at ambient temperature 20-25°C, normal atmospheric pressure, and air humidity not exceeding 80%. The IR spectra were processed using SpectraLUM software, version 2.0.1.295.

^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-ECX400 spectrometer (9.39 T, 100.5 MHz) in DMSO-d_6 and D_2O. The spectra were processed using ACD/Labs Release 12, ver. 12.01 (Build 39104) and MestReNova, ver. 14.2.1-27684.

Hydrolysis of MC was performed as follows: 1 g of cellulose ether and 30 mL of 5% perchloric acid solution were boiled in a flask with a reflux condenser under magnetic stirring for 5 h. After completion of the reaction, the mixture was neutralized with potassium hydroxide to a neutral medium; potassium perchlorate was filtered off during evaporation on a rotary evaporator; the completely evaporated sample was dissolved in 1 mL of D_2O, centrifuged, and analyzed by ^{1}H and ^{13}C NMR spectroscopy.

To determine the degree of polymerization of cellulose, a method based on the dependence of the intrinsic viscosity of a cellulose solution in a copper (II) – ethylenediamine complex on its molecular weight was used (European Pharmacopoeia, 2021). The degree of polymerization (DP) was calculated using the Mark–Houwink–Sakurada equation with constants established for this solvent-polymer system.

The dynamic viscosity of the obtained MC samples was determined for 2% aqueous solutions using a Brookfield DV-II+PRO rotational viscometer (manufactured by Brookfield Engineering Laboratories, Inc., USA), using spindle LV-1 at a fixed rotation speed of 10 rpm.

Gas chromatographic analysis was performed using a Thermo Scientific Trace 1310 gas-liquid chromatograph (Thermo Scientific, USA) equipped with a quadrupole mass spectrometric detector. Separation was achieved on a 30 m × 0.25 mm quartz capillary column from RESTEK (USA) with a stationary phase Rxi®-5ms. Samples (1.0 μL) were injected in a split mode (1:30) with helium as the carrier gas at a flow rate of 1.2 mL/min. The oven program consisted of an initial column oven temperature of 50°C (5 min hold time), a ramp of 10°C/min, and a final oven temperature of 250°C (8 min hold time). Detection was performed with an ISQ LT mass spectrometer (Thermo Scientific, USA), operating with electron impact ionization at 70 eV, interface temperature 230°C, source temperature 200°C, scan range 43-550 amu, and a solvent delay of 1 min. Data analysis and processing were performed using Xcalibur software package and the NIST 11 database (25.03.2020).

3. Results and Discussion

The hemp used in this study contained 45.0% cellulose, 27.5% hemicellulose, 11.5% lignin, and 5% ash. The hemp was treated with an aqueous solution of acetic acid with addition of hydrogen peroxide (method A) (Hao et al., 2020) or an aqueous solution of sodium hydroxide and ammonia (method B) (Valishina et al., 2015).

3.1 Preparation of cellulose by the organosolv method (Method A)

50 g of hemp was placed into a 1 L flask equipped with a reflux condenser and an anchor-type stirrer. Then, 390 mL of glacial acetic acid, 210 mL of distilled water, and 6 mL of 30% hydrogen peroxide solution were added. The mixture was heated under reflux in a water bath at 85-90°C for 3 h with stirring. After cooling to room temperature, the precipitate was collected by filtration on a Büchner funnel and washed successively with 50% aqueous acetic acid (2 × 100 mL), tap water until neutral (approx. 700-1000 mL), and distilled water (200 mL). The resulting precipitate was transferred into a 1 L beaker containing 500 mL of 5% sodium hydroxide solution, heated to 60-70°C, and stirred for 1 h. After cooling to room temperature, the precipitate was filtered on a Büchner funnel and washed with distilled water until neutral, as indicated by universal indicator paper. The precipitate was then suspended in 200 mL of ethanol and filtered. It was dried in an oven at 60-70°C to constant weight, followed by drying at 105°C for 1 h. A light-cream fibrous mass weighing 29 g was obtained.

3.2 Preparation of cellulose by the sodium hydroxide-ammonia method (Method B)

50 g of hemp was placed in a 1 L flask equipped with a reflux condenser and an anchor-type stirrer; an aqueous solution consisting of 500 mL of distilled water, 20 g of sodium hydroxide, and 20 mL of 25% ammonia solution was added. The flask with the reflux condenser was heated with stirring: kept for 1 h at 30-45°C, and the temperature was then increased to 85-90°C and heating was continued for 5 h. After cooling to room temperature, the precipitate was filtered, then washed several times with hot water until neutral (universal indicator paper), and finally washed with distilled water (200 mL). The obtained precipitate was suspended in 200 mL of ethanol and filtered. It was dried in an oven at 60-70°C till the weight was constant, then at 105°C for 1 h. Finally, 30 g of a light-cream fibrous mass was obtained.

3.3 Determination of the degree of polymerization

The degree of polymerization (DP) of the obtained cellulose samples was determined by a viscometric method using cupriethylenediamine (CED) solution (European Pharmacopoeia, 2021; ISO, 2010; TAPPI, 2013). The method is based on measuring the flow time of the dilute cellulose solution through a calibrated capillary viscometer and subsequent calculation of the intrinsic viscosity, which correlates with the number-average degree of polymerization.

A CED solution with a concentration of 1.0±0.02 M in copper ions and 2.0 M in ethylenediamine was prepared as described in Appendix B of TAPPI (2013) or Appendix A of ISO (2010). The copper content in the CED solution, determined by complexometric titration with EDTA, was 1.00±0.02 mol/L.

A sample of cellulose was pre-dried at a temperature not exceeding 60°C to constant weight. An exact weight of absolutely dry sample (0.25 g) was placed in a conical flask, and 25 mL of distilled water was added. The suspension was intensively stirred for 2 min to ensure uniform swelling of the fibers. Then the flask was purged with nitrogen, and 25 mL of the 1 M solution of bis(ethylenediamine)copper (II) were added, after which the flask was tightly closed. The mixture was stirred with a stirrer until the cellulose was completely dissolved; the dissolution time was 1.5 h. Complete dissolution was checked by filtering the obtained solution through a glass filter (pores 40-100 μm) – the absence of a gel-like residue indicated complete dissolution.

Measurements were carried out using a capillary glass viscometer VPH-4 with a capillary diameter of 0.62 mm at a constant temperature of 25±0.1°C. The viscometer was previously calibrated with glycerol. The flow time of the solvent (1 M CED diluted 1:1 with distilled water) and the investigated cellulose solution were measured at 25.0±0.1°C with an electronic stopwatch accurate to 0.1 s. Each measurement was performed at least three times and the arithmetic mean flow time t (s) was calculated.

3.3.1. Calculation of degree of polymerization

The relative viscosity η_{rel} was calculated using formula (1):

$$\eta_{rel} = \frac{t}{t_0} \quad (1)$$

where t is the average flow time of the cellulose solution (s); t_0 is the average flow time of the pure solvent (0.5 M CED) (s).

From the obtained η_{rel} value, the product of the intrinsic viscosity [η] and the mass concentration of the polymer was determined using the “Intrinsic Viscosity Table” from ASTM D 1795 (ASTM, 2010). The intrinsic viscosity [η] (mL/g) was calculated by dividing this product by the concentration of cellulose in the solution c (g/dL).

The degree of polymerization (DP) was calculated using the simplified formula (2) recommended by ASTM D 1795:

$$DP = 190 \times [\eta] \quad (2)$$

where 190 is the empirical coefficient for the cellulose-CED system at 25°C; and [η] is the intrinsic viscosity.

The degree of polymerization of cellulose obtained by method A was 930, and by method B – 851.

Next, the effect of alkaline treatment conditions on the degree of polymerization of cellulose was studied. In the preparation of cellulose ethers, in particular methylcellulose, a key step is the preliminary activation of cellulose, which involved treatment with a concentrated sodium hydroxide solution. During mercerization, both supramolecular transformations (transition of cellulose I to cellulose II, swelling, increased availability of hydroxyl groups) and degradative processes – cleavage of glycosidic bonds leading to a decrease in the degree of polymerization (DP) – occur. Therefore, studying the effect of NaOH concentration and treatment time on the DP of cellulose is a necessary step for the scalable and controlled production of cellulose ethers with desired properties.

Cellulose was mercerized at a constant temperature (25°C), varying the sodium hydroxide solution concentration (20, 25, 30, 35, 40, 45%) and the treatment duration (30, 60, 90, 120 min). The ratio of cellulose to alkali solution was as follows: 20 mL of alkali solution per 1 g of cellulose. After soaking the cellulose in the alkali solution and holding for the required time, excess alkali solution was removed from the reaction mixture by pressing, and diluted with 100 mL of distilled water, neutralized with acetic acid, filtered, washed with distilled water, and dried in an oven at 60-70°C to constant weight and then additionally at 105 °C for 1 h. The degree of polymerization of the cellulose samples was determined by the viscometric method as described above. The effect of the grinding process after mercerization on the degree of polymerization of cellulose was also studied. For this purpose, after squeezing out the excess alkali, the obtained sample was ground in a conventional kitchen blender for 5 min, then neutralized with acetic acid and treated as described above. The degree of polymerization of the cellulose samples was determined by the viscometric method as described above. The data are shown in Tables 1 and 2.

Analysis of the obtained data shows that the highest degree of cellulose degradation (in terms of reduction in the degree of polymerization, DP) is observed with the use of a 30% sodium hydroxide solution in both cases. For example, for cellulose obtained by method A, after alkaline treatment with 30% NaOH, the DP reduction reaches 22%, and after subsequent milling – 58%. At lower (20%) and higher (40-50%) NaOH concentrations, the degradation effect is weaker, indicating a non-monotonic (extreme) nature of the "concentration–degradation degree" relationship. Increasing the duration of alkaline treatment from 30 to 120 min in all studied concentrations leads to a consistent decrease in DP. The most intensive DP reduction occurs during the first 60 min of treatment, after which the degradation rate slows down considerably. This behavior is explained by the preferential destruction of amorphous regions of cellulose at the initial stage, whereas crystalline domains exhibit higher resistance to the action of alkali. Mechanical milling after alkaline treatment causes a much more pronounced DP reduction compared to chemical treatment alone. Depending on the conditions of alkaline treatment, the DP reduction under the action of alkali alone ranges from 3 to 22%, whereas after milling this value increases to 37-61%. Moreover, the milling effect dominates over chemical factors: even under the mildest conditions (20% NaOH, 30 min), milling leads to a DP reduction of 42-49%, which significantly exceeds the degradation caused by the treatment itself. A similar effect has been described (Gao, 2021) for cellulose derived from wheat straw.

Table 1. Effect of alkaline treatment on the degree of polymerization (DP) of cellulose. Organosolv treatment (Method A). Initial DP = 930.

NaOH Concentration (%)	Treatment Time (min)	DP after Treatment	DP Reduction after Treatment* (%)	DP after Treatment + Grinding	DP Reduction after Grinding* (%)
20	30	898	4	561	40
20	60	866	7	515	45
20	90	845	9	491	47
20	120	835	10	445	52
30	30	835	10	522	44
30	60	782	16	485	48
30	90	751	19	451	52
30	120	730	22	386	58
40	30	887	5	584	37
40	60	835	10	529	43
40	90	803	14	489	47
40	120	782	16	446	52
50	30	887	5	587	37
50	60	864	7	533	43
50	90	845	9	463	50
50	120	830	11	423	55

* DP reduction is calculated as $((930 - DP_{exp}) / 930) \times 100\%$, rounded to the nearest integer.

Table 2. Effect of alkaline treatment on the degree of polymerization (DP) of cellulose. Soda-ammonia treatment (Method B). Initial DP = 851.

NaOH Concentration (%)	Treatment Time (min)	DP after Treatment	DP Reduction after Treatment* (%)	DP after Treatment + Grinding	DP Reduction after Grinding* (%)
20	30	826	3	496	42
20	60	796	6	451	47
20	90	776	8	434	49
20	120	767	10	401	53
30	30	767	10	493	42
30	60	718	16	443	48
30	90	688	19	401	53
30	120	678	20	336	61
40	30	816	4	528	38
40	60	776	8	477	44
40	90	767	9	429	50
40	120	757	11	395	54
50	30	816	4	525	38
50	60	796	6	469	45
50	90	776	8	413	51
50	120	767	9	388	54

* DP reduction is calculated as $((851 - DP_{exp}) / 851) \times 100\%$, rounded to the nearest integer.

3.4. Mercerization of cellulose

4 g of cellulose obtained by method A or B were treated with 20 mL of an aqueous sodium hydroxide solution of various concentrations according to Table 2. The suspension of cellulose in alkali was intensively stirred at room temperature for 2 h. After treatment, the cellulose was filtered and squeezed. 12-14 g of mercerized cellulose were obtained, which was immediately used in the reaction.

3.5. Methylation of cellulose, fractionation, and characterization by IR and NMR

13 g of mercerized cellulose were placed in a 250 mL round-bottom flask equipped with a mechanical anchor-type stirrer with a sealed Teflon gland and a reflux condenser; a mixture consisting of 30 mL of toluene and 12 mL of isopropanol was added. To the resulting suspension, with stirring, dimethyl sulfate was added dropwise over 30 min (a series of experiments was carried out using 3 mL (variant 1), 4 mL (variant 2), 5 mL (variant 3), 6 mL (variant 4), and 7 mL (variant 5) of dimethyl sulfate) dissolved in a mixture of 3 mL of toluene and 1.2 mL of isopropanol. Then the reaction mixture was stirred for 1 h at 35-40°C, then for 1 h at 40-50°C, and for 3 h at 50-60°C. After cooling to room temperature, the precipitate was filtered on a Büchner funnel. The obtained precipitate was placed in a beaker and neutralized under cooling to 0-5°C with a solution of acetic acid in isopropanol (20 wt% acid) to pH 3-4 (about 20 mL required) and immediately filtered. The precipitate on the filter was washed with 20 mL of a 5:1 by volume mixture of isopropanol and water. The product was dried in air for 24 h. 5.1-6.5 g of product were obtained. Then the obtained product was tested for water solubility. For this, all methylcellulose obtained in the experiment was dissolved in 250 mL of distilled water: the water was heated to 80°C, the methylcellulose powder was added with stirring, stirred at this temperature for 2 h for better swelling and wetting, then the heating was turned off and the solution was stirred at room temperature for 24 h. Then the precipitate was filtered, dried, and weighed. The resulting solution was evaporated in vacuum, dried, and weighed. As a result, two fractions of methylcellulose were obtained, which were studied by IR spectroscopy (Figure 1).

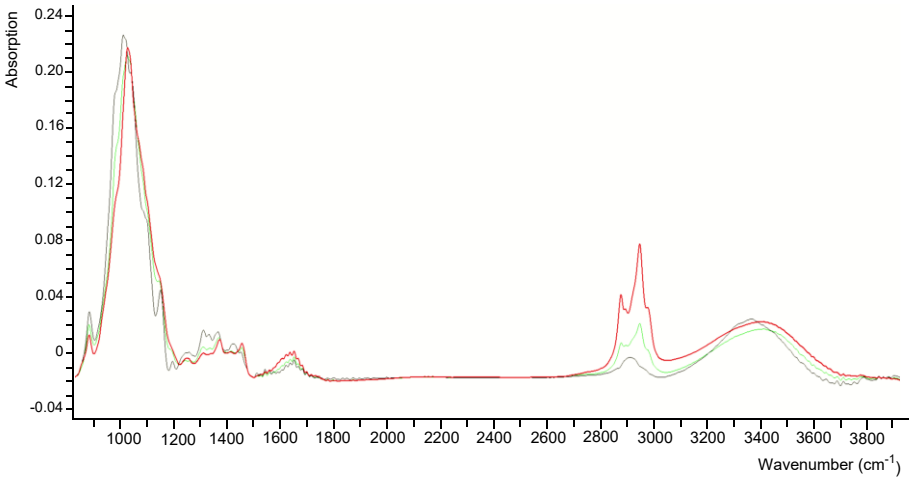


Figure 1. IR spectra of initial cellulose (black line), water-soluble product (red line), and water-insoluble product (blue line) (variant 5a)

The main difference between the IR spectra of methylcellulose and cellulose is due to the chemical modification, namely the substitution of hydroxyl groups with methoxy groups. This leads to several characteristic changes in the spectrum. In particular, a weakening of the O–H stretching band – the intensity of the broad band around ~3400 cm^{-1} decreases significantly due to the decrease in the number of free OH groups, which is the main sign of successful substitution, and an intensification of the C–H stretching bands in the region 2800–3000 cm^{-1} – the intensity of the peaks corresponding to C–H bonds increases significantly, which is caused by the appearance of methoxy substituents (Viera et al., 2007). There are also changes in the "fingerprint" region: the spectral region from 1500 to 800 cm^{-1} undergoes significant changes, which also confirms the fact of chemical modification and changes in the polymer structure. The water-soluble fraction of methylcellulose was further studied by ^{1}H and ^{13}C NMR spectroscopy in DMSO-d_6.

A typical ^{1}H NMR spectrum of methylcellulose in DMSO-d_6 is shown in Figure 2. The assignment of signals in the ^{1}H NMR spectrum was made on the basis of the work of Kono et al. (2017). Identification of the water signal in the mixture of sample and DMSO-d_6 was carried out by adding water: an increase in the integral intensity of the signal at 3.05 ppm was observed, as well as the disappearance of the hydroxyl proton signals at 4.57, 4.69, and 5.01 ppm due to accelerated proton exchange.

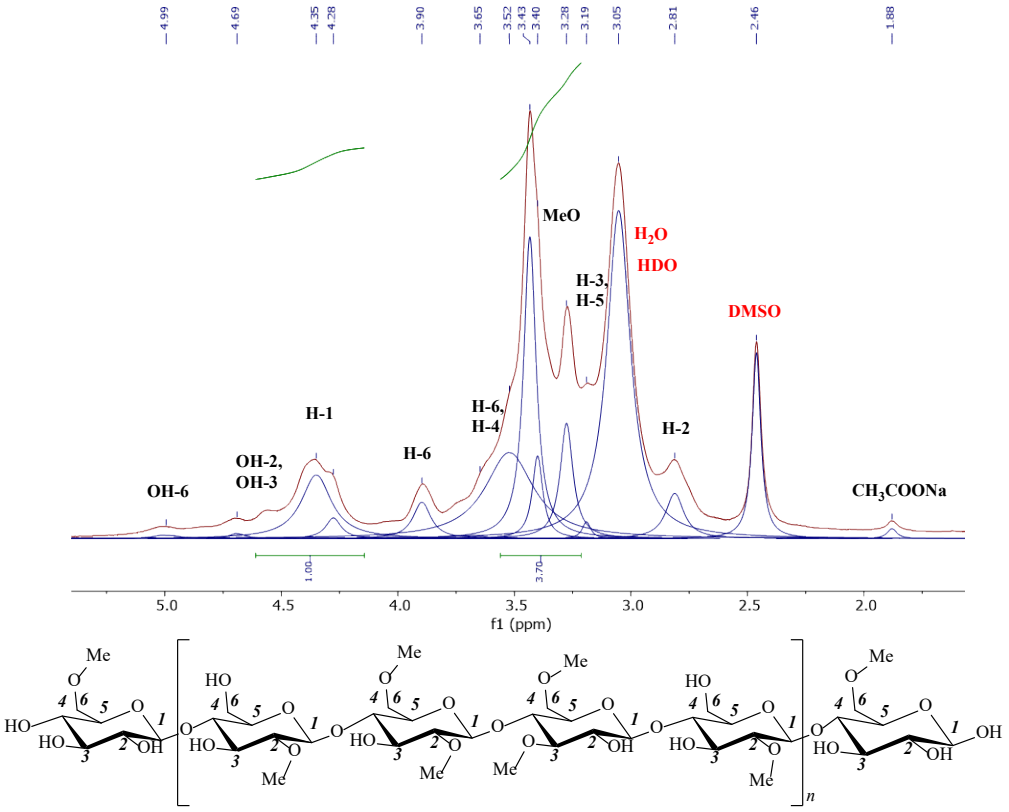


Figure 2. ^{1}H NMR spectrum (DMSO-d_6) of a water-soluble methylcellulose (sample 4a); calculated degree of substitution 1.233, and the structural formula of methylcellulose.

Since methylcellulose is a polymer with a high molecular weight, slow molecular mobility is observed and, as a consequence, broadening of signals due to shortened transverse relaxation time (T_2). The signals of the anhydroglucose ring protons (H-2,3,4,5,6) and methoxy groups (OCH_3) overlap in the region 3.0–4.0 ppm, forming a multiplet cluster that cannot be resolved even at high instrument resolution. In addition, the residual water signal in DMSO-d_6 overlaps with the signals of the anhydroglucose fragment protons. Even after thorough drying of the sample and solvent, traces of water cannot be completely removed, and the use of water signal suppression methods often leads to distortion of the integral intensities of adjacent polymer signals. Therefore, to accurately estimate the integral intensities of signals, spectrum deconvolution was used. This is an interactive process in which the software fits theoretical lines (by default, Generalized Lorentzian) to approximate the experimental spectrum. The degree of substitution from the ^{1}H NMR spectrum was determined by the ratio of the total intensity of the methoxy group signals to the intensity of the H-1 hydrogen atoms signals multiplied by three (formula 3). When using ^{13}C NMR data, the degree of substitution was calculated as the ratio of the sum of the intensities of the methoxy group carbon signals to the total intensity of the acetal carbon C-1 signals (formula 4).

$$DS = \frac{I_{MeO}}{3\sum I_{C1-H}} \quad (3)$$

$$DS = \frac{I_{Me}}{\sum I_{C1}} \quad (4)$$

To verify the obtained results, a comparison was made with the results obtained from ^{13}C NMR spectra. It should be noted that recording ^{13}C NMR spectra requires a significant acquisition time. In the work of Kono et al. (2017), this time was 6 h, whereas in the present study an experiment with an acquisition time of 8 h was used. Figure 3 shows the ^{13}C NMR spectrum of methylcellulose (sample 5). The degree of substitution (DS) was determined as the ratio of the intensity of the peaks at 58-62 ppm (methoxy group signals) to the intensity of the peak at 101-104 ppm (C-1 carbon signals).

Thus, the DS values determined by ^{1}H NMR spectroscopy are in good agreement with the results obtained from ^{13}C NMR spectra. It should be noted that recording ^{1}H NMR spectra is technically a simpler task.

Then, to determine the degree of substitution, a method including preliminary acid hydrolysis of the cellulose ether was tested (Ye & Farriol, 2007; Araslankin et al., 2019; Kostryukov et al., 2020a,b). For partial hydrolysis, 250 mg of methylcellulose sample was suspended in 15 mL of distilled water, 200 µL of 70% perchloric acid were added, and the mixture was heated with stirring using a magnetic stirrer at 100°C for 3 h. After that, the reaction mixture was neutralized with 10% KOH solution, the precipitated potassium perchlorate was filtered off, the filtrate was evaporated to a volume of 5 mL, then the potassium perchlorate was filtered off again and the filtrate was evaporated to dryness. To obtain dry residue, 1 mL of D_2O was added, centrifuged, and 800 µL of the supernatant was taken for NMR study.

Figure 4 shows the ^{1}H NMR spectrum of methylcellulose (sample 5a) after partial hydrolysis, recorded in D_2O at 25°C and 70°C. Recording the spectrum at 70°C was aimed at separating the signals of water protons and H-1 atoms, which made it possible to avoid using the water signal suppression technique. The use of the latter is undesirable because it can lead to distortion of signal intensities, making quantitative studies impossible.

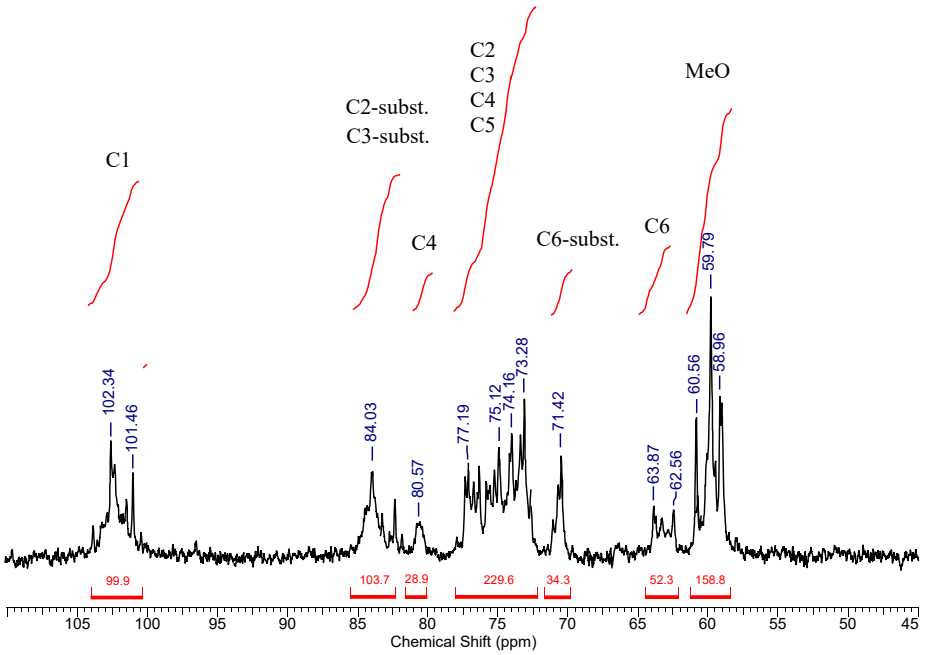


Figure 3. ^{13}C NMR spectrum (DMSO-d_6) of a water-soluble methylcellulose (sample 5a); calculated degree of substitution 1.59.

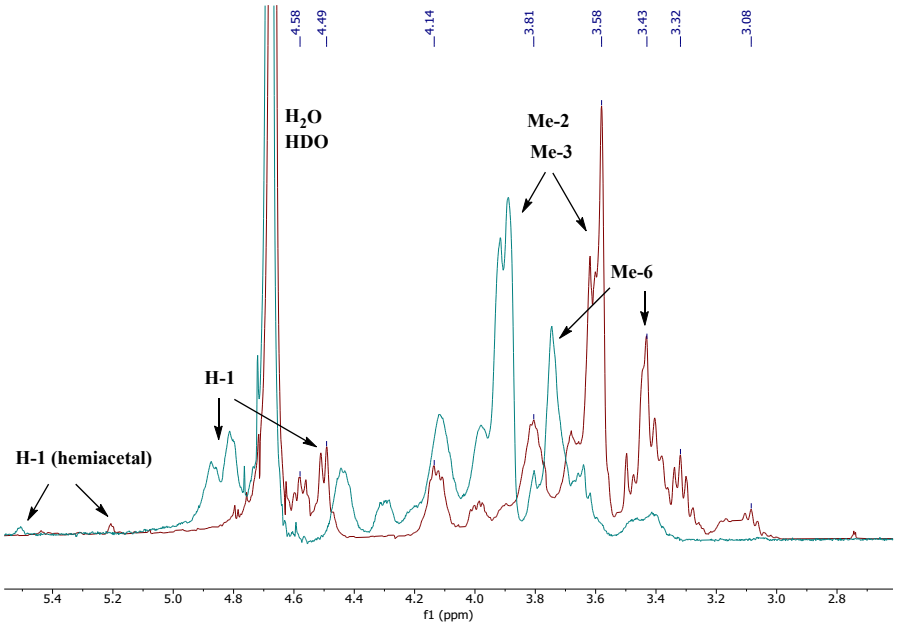


Figure 4. ^{1}H NMR spectra (D_2O) of a water-soluble methylcellulose (sample 5a) after acid hydrolysis: at 25°C (red line) and 70°C (blue line).

As shown in the figure, when recording the ^{1}H NMR spectrum at 70°C, it is possible to separate the signals of H-1 and water protons, but the line resolution in the multiplets deteriorates. This is due to a decrease in the spin-lattice relaxation rate with increasing temperature, as well as coagulation of methylcellulose at temperatures above 60°C. However, compared with the ^{1}H NMR spectrum obtained in DMSO-d_6, the resolution in water is much higher. Figure 5 shows the ^{1}H NMR spectrum recorded at 75°C, with signal assignment and integration of the regions necessary for calculating the degree of substitution. The following temperature dependence was observed: with increasing temperature, the chemical shifts drift downfield by about 0.30-0.33 ppm. In the MC spectrum after acid hydrolysis, a low-intensity signal appears at ~5.2 ppm (25°C) and ~5.5 ppm (70°C), which belongs to the H-1 atom at the hemiacetal carbon. Using the intensities of the H-1 signals at the acetal and hemiacetal carbons, the degree of polymerization of the polysaccharide can be calculated. In our case, the degree of polymerization of the methylcellulose sample after acid hydrolysis was 45. The ^{13}C NMR spectra of partially depolymerized methylcellulose samples recorded in D_2O are similar to the spectra obtained for solutions in DMSO-d_6 (Figure 6).

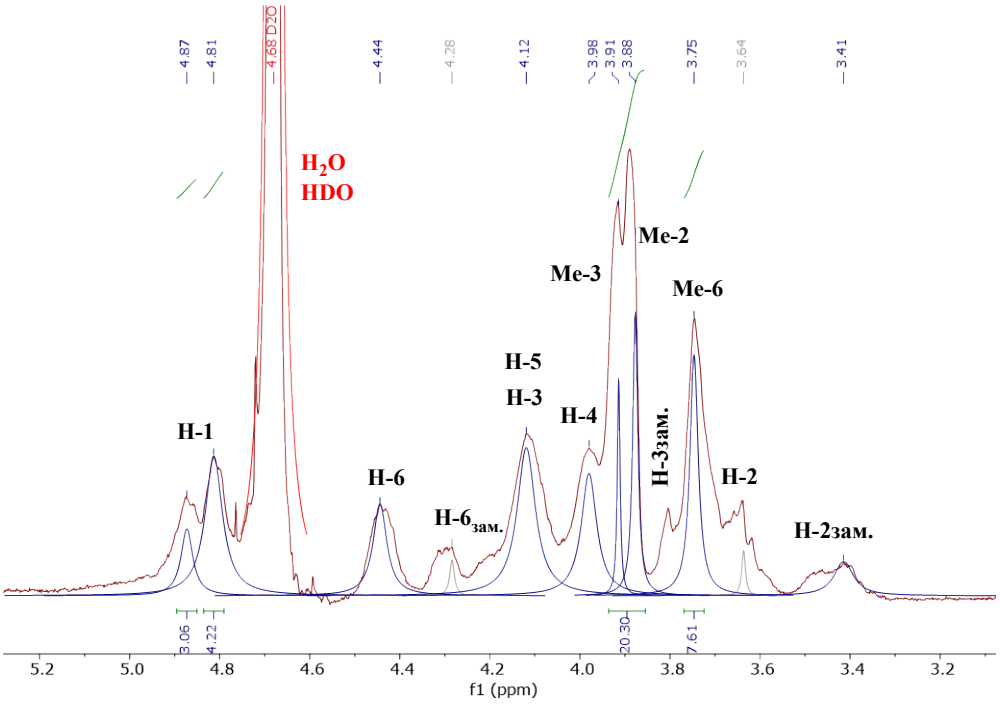


Figure 5. ^{1}H NMR spectrum of partially depolymerized methylcellulose in D_2O (sample 4a), calculated degree of substitution 1.28.

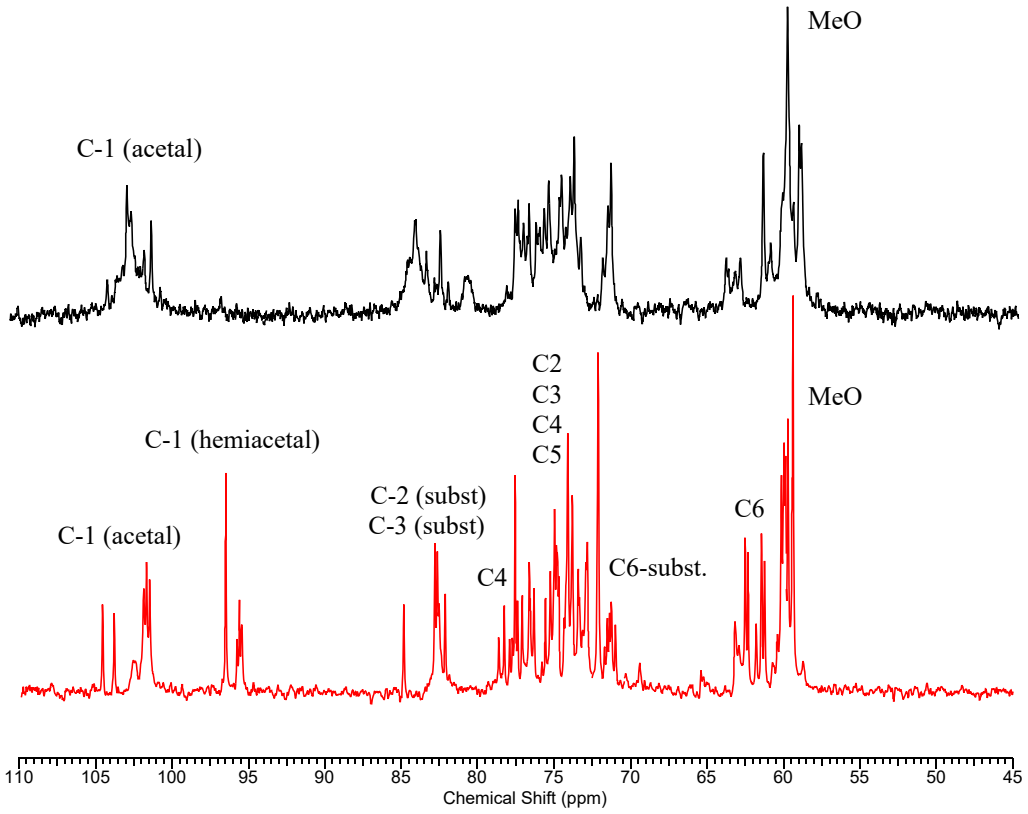


Figure 6. ^{13}C NMR spectra of methylcellulose (sample 5a) after partial hydrolysis with perchloric acid in D_2O (red line) and DMSO-d_6 (black line).

Then, the obtained DS values for methyl groups were recalculated into the percentage content of methoxy groups (X_{MeO}) using formula (5), where M_0 is the molecular weight of the methylcellulose repeating unit calculated taking into account the degree of substitution. The formula of the methylcellulose repeating unit is $C_6H_7O_2(OCH_3)_m(OH)_{3-m}$, where m is the degree of substitution by methoxy groups. M_0 = 162 – 17m + 31m = 162 + 14m.

$$X_{MeO} = \frac{31m \times 100\%}{M_0} \quad (5)$$

The obtained values for the methoxy group content were compared with the values obtained by gas-liquid chromatography (GLC) analysis.

3.6. Description of the GLC analysis method

Accurate weights of 50 mg of methylcellulose and 500 mg of potassium iodide were placed into chromatographic vials, then, using a micropipette, accurate volumes of 20 μL of heptane (internal standard), 500 μL of 80% phosphoric acid, and 500 μL of p-xylene were

added. The vials were tightly closed and thermostatted at 130°C for 1 h, after which they were analyzed chromatographically.

In a similar manner, using a stock solution containing 50 mg of absolute methanol in 1 mL of p-xylene, standard samples were prepared. For this, 500 mg of potassium iodide were placed into each vial, then accurate volumes of 20 μL of heptane and 500 μL of 80% phosphoric acid were added. 500 μL of the stock solution were added to vial No. 1, 300 μL of stock solution and 200 μL of p-xylene were added to vial No. 2, and so on. Thus, a set of standards corresponding to methanol concentrations of 1.563, 0.781, 0.312, 0.156, 0.078, 0.049 mmol/mL (50, 25, 10, 5, 1, 0.1, 0.01 mg/mL) was obtained. The vials were tightly closed, thermostatted, and analyzed as described above.

Using the obtained results, a calibration graph of the peak area ratio of iodomethane to heptane versus the concentration of iodomethane, which is numerically equal to the concentration of the original methanol, was plotted (Figure 7).

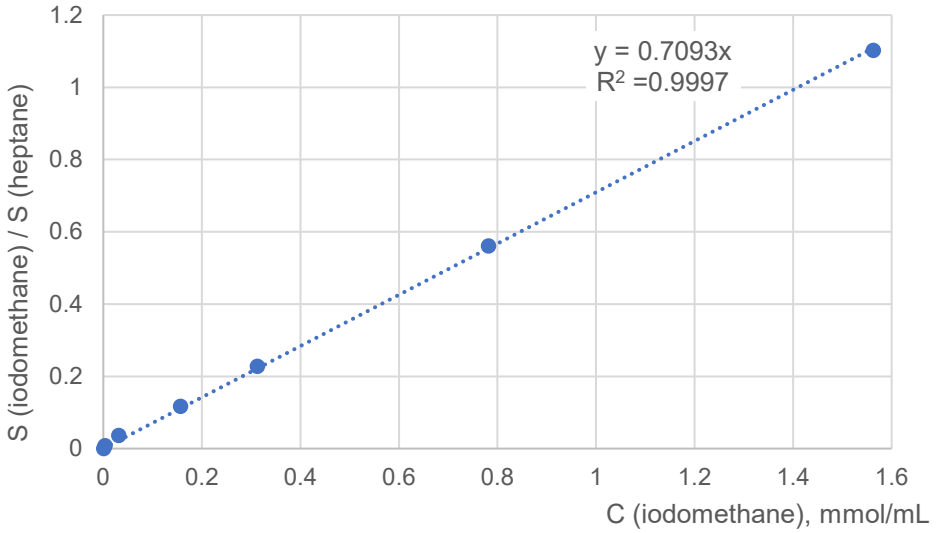


Figure 7. Calibration graph using the internal standard method.

Based on the chromatography results and the linear regression equation for the graph in Figure 7, the response factor R was determined as the slope of the calibration line, and then the relative content of methoxy groups in the modified polymer samples was calculated using formula (6), where S_1 is the peak area of the internal standard on the chromatogram of the test solution; S_0 is the peak area of iodomethane on the chromatogram of the test solution; R is the response factor; V is the volume of the organic phase in the test solution (mL); M is the molar mass of the methoxy group (31.0); m is the weight of the test sample (calculated as dry matter) in the test solution (mg).

$$\omega(CH_3O) = \frac{S_1 * R * V * M}{S_0 * m} * 100\%, \quad (6)$$

Table 3 presents the experimental design, including NaOH concentration, mercerization time, the molar ratio of initial cellulose to dimethyl sulfate, water solubility of

the product, and the methoxy group content determined for methylcellulose samples after dialysis but not fractionated into water-soluble and water-insoluble fractions.

Table 3. Cellulose methylation parameters, product characteristics, degree of substitution, and methoxy group content

№	Alkali Treatment Conditions, C(NaOH), % (time 120 min)	Molar Ratio (cellulose : DMS)	Water-soluble Fraction* (%)	Water-insoluble Fraction* (%)	Substitution Parameters of Non-fractionated MC Samples after Dialysis*		
					^{1}H NMR Spectrum of Hydrolysate		GLC Analysis, Methoxy Content (%)
					DS	Methoxy Content (%)	
1a	20	1 : 1.28	25 / 12	75 / 88	0.65 / 0.47	11.78 / 8.61	11.42 / 8.33
2a		1 : 1.71	36 / 17	64 / 79	0.80 / 0.59	14.39 / 10.81	13.95 / 10.51
3a		1 : 2.13	52 / 31	48 / 69	1.03 / 0.73	18.07 / 13.21	17.52 / 12.79
4a		1 : 2.56	71 / 45	29 / 55	1.29 / 0.93	22.27 / 16.47	21.60 / 15.99
5a		1 : 2.99	95 / 58	5 / 42	1.59 / 1.11	26.75/19.41	26.55 / 18.85
1b	30	1 : 1.28	25 / 11	75 / 89	0.65 / 0.45	11.78 / 8.36	11.39 / 8.16
2b		1 : 1.71	37 / 23	63 / 77	0.82 / 0.62	14.62 / 11.3	14.18 / 10.91
3b		1 : 2.13	59 / 41	41 / 59	1.13 / 0.87	19.64 / 15.55	19.05 / 15.08
4b		1 : 2.56	76 / 39	26 / 61	1.36 / 0.85	23.35 / 15.09	22.65 / 14.61
5b		1 : 2.98	95 / 45	5 / 55	1.60 / 0.93	26.90 / 16.47	26.36 / 16.05
1c	40	1 : 1.28	33 / 16	67 / 84	0.76 / 0.47	13.68 / 8.61	13.29 / 8.32
2c		1 : 1.71	42 / 28	58 / 72	0.89 / 0.69	15.78 / 12.49	15.31 / 12.15
3c		1 : 2.13	65 / 43	35 / 57	1.21 / 0.90	20.96 / 16.01	20.33 / 15.54
4c		1 : 2.56	79 / 55	21 / 45	1.41 / 1.07	23.99 / 18.74	23.27 / 18.21
5c		1 : 2.98	100 / 65	0 / 35	1.70 / 1.21	28.36 / 20.96	27.49 / 20.36
1d	50	1 : 1.28	33 / 19	67 / 81	0.76 / 0.51	13.68 / 9.35	13.30 / 9.11
2d		1 : 1.71	45 / 30	55 / 70	0.93 / 0.72	16.47 / 12.97	15.98 / 12.56
3d		1 : 2.13	71 / 46	29 / 54	1.29 / 0.94	22.27 / 16.7	21.62 / 16.21
4d		1 : 2.56	84 / 61	16 / 39	1.48 / 1.15	25.05 / 20.08	24.30 / 19.45
5d		1 : 2.98	100 / 77	0 / 23	1.75 / 1.38	29.09 / 23.56	28.76 / 22.86

Note. The first value corresponds to cellulose obtained by the organosolv method (method A), the second value after the slash corresponds to cellulose obtained by the sodium hydroxide-ammonia method (method B).

Analysis of the data in Table 3 reveals a clear regularity due to an increase in the amount of DMS introduced into the reaction: the degree of substitution increases monotonically, the methoxy group content also increases, and the proportion of the

water-soluble fraction increases, which is generally expected. Thus, increasing the molar ratio of DMS to cellulose is the main factor in increasing the degree of substitution and, consequently, the water solubility of the product.

The influence of NaOH concentration during mercerization (at a fixed cellulose : DMS ratio) is more complex and non-monotonic. Consider, for example, the ratio 1:2.99 (maximum amount of DMS) at different alkali concentrations:

- 20% NaOH: DS = 1.11; water-soluble fraction 58%;
- 30% NaOH: DS = 0.93; water-soluble fraction 45%;
- 40% NaOH: DS = 1.21; water-soluble fraction 65%;
- 50% NaOH: DS = 1.38; water-soluble fraction 77%.

It can be seen that at 30% NaOH there is a drop – the degree of substitution and solubility are lower than at 20% and 40-50%. When analyzing the effect of alkaline treatment on the degree of polymerization of cellulose, it was observed that the maximum degradation of cellulose occurs precisely at 30% NaOH. However, the decrease in DS at 30% NaOH is not associated with cellulose degradation, but with a change in the supramolecular structure of cellulose: the transition from cellulose I to cellulose II, which has a lower reactivity. At higher NaOH concentrations (40-50%), the water activity decreases, swelling is limited, but a more complete deprotonation of the hydroxyl groups of cellulose occurs due to higher pH values, which ultimately gives a higher degree of substitution.

Thus, the optimal NaOH concentration for mercerization in this synthesis is 50% (maximum DS and solubility).

The use of cellulose obtained by the organosolv method consistently leads to the production of methylcellulose (MC) with a higher degree of substitution (DS) and, as a consequence, better solubility. This is explained by a combination of factors: organosolv treatment is a milder delignification method than harsh sodium hydroxide-ammonia cooking; the cellulose obtained in this case has a higher molecular weight (DP) and, critically, a lower degree of crystallinity. This makes its fibrils more “loose”, opening up more hydroxyl groups (–OH) for interaction with sodium hydroxide.

The systematically lower values of methoxy group content determined by the GLC method compared to the NMR data (by 0.2-0.7% abs.) can be attributed to two main factors. First, the possible presence of residual moisture in the non-fractionated methylcellulose samples after dialysis. It is known that methylcellulose is hygroscopic, and the presence of crystalline water increases the actual weight of the sample without contributing to the methoxy group content, which leads to an underestimation of the calculated mass percentage in GLC analysis. Nevertheless, both analytical methods give close values, which confirms the correctness of the DS calculations.

Thus, to obtain methylcellulose with good water solubility (soluble fraction more than 70%) and a degree of substitution above 1.3 (which corresponds to a methoxy group content of about 22-28%), it is necessary to use: a NaOH solution for mercerization of at least 40%; a molar ratio of cellulose to DMS of at least 1 : 2.5-3.0; and the more reactive organosolv cellulose.

4. Conclusions

Laboratory methods for the synthesis of methylcellulose from cellulose isolated from industrial hemp using dimethyl sulfate as a methylating agent have been developed and optimized. The following were established:

- Two methods for isolating cellulose from hemp were compared: the organosolv (method A) and sodium hydroxide-ammonia (method B). The organosolv method provided cellulose with a higher degree of polymerization (930 vs 851) and a lower degree of crystallinity, which made it more reactive in subsequent methylation.
- The effect of mercerization conditions (NaOH concentration 20-50%, treatment time 30-120 min) on the degree of polymerization of cellulose was studied. Maximum alkaline degradation was observed at 30% NaOH; higher concentrations (40-50%) limited swelling but promoted more complete deprotonation of OH groups.
- The influence of the molar ratio of cellulose to dimethyl sulfate (from 1:1.28 to 1:3) and NaOH concentration on the degree of substitution (DS) and water solubility of the final MC was investigated. A non-monotonic dependence of DS on alkali concentration was found: minimum at 20-30% NaOH, maximum at 50% NaOH.
- Optimal synthesis conditions ensuring a DS ≥ 1.3 and a water-soluble fraction >70% are: mercerization with 50% NaOH, a cellulose : DMS molar ratio of 1:2.5-3.0, and the use of organosolv cellulose. Under these conditions, MC with DS = 1.38-1.70 and a methoxy group content of 23.6-28.4% was obtained.
- A convenient GLC method for the determination of methoxy groups in MC was developed, which correlates well with NMR data; the slight underestimation by GLC is explained by residual moisture in the samples.

The results obtained allow us to recommend industrial hemp as a promising renewable raw material for the synthesis of water-soluble cellulose ethers.

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6. Authors' Contributions

S.G. Kostryukov designed research;
Sh.A. Fayzrakhmanov and A.A. Burtasov performed research;
V.A. Kalyazin analyzed data;
A.A. Burtasov and V.A. Kalyazin contributed new reagents/analytic tools;
S.G. Kostryukov coordinated research;
S.G. Kostryukov, Sh.A. Fayzrakhmanov, A.A. Burtasov, and V.A. Kalyazin wrote the paper.

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7. Conflicts of Interest

The authors of this work declare that they have no conflict of interest.

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