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Reactivity of Poly-, Di-, and Monosaccharides in Their Hydrolysis in Subcritical Water

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Abstract—The reactivity of the water-soluble sodium salt of carboxymethyl cellulose (CMC), sucrose, glucose, and fructose in subcritical water at 120–320°C is reported. A mathematical model is suggested to describe the variation of the CMC molar mass during hydrolysis at various temperatures and reaction times. Kinetic parameters of the conversions of CMC, sucrose, glucose, and fructose in subcritical water are presented. High temperatures and short reaction times are favorable for the formation of monosaccharides from CMC.

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Cellulose is a linear monosaccharide consisting of D-glucose monomer units joined together by β-1,4-glycosidic linkages. Native celluloses can be considered in terms of an amorphous–crystalline structural model with a two-phase crystalline component [1, 2]. Cellulose monomers, oligomers, and deep conversion products (oligosaccharides, glucose, furfurals, and others) are valuable substance usable in the production of food, medicines, etc. The most promising way of obtaining these non-macromolecular products is cellulose hydrolysis.

The present-day wood hydrolysis technology employs mineral acids and alkalis as catalysts. For creating new, environmentally friendly technologies for this important process, it is essential to study reactions of cellulose in subcritical and supercritical water (sc-H_2O). The results of such studies might provide scientific foundations for sustainable processing of cellulose-containing raw materials, including technogenic formations and agricultural and wood processing waste [3]. The physical and chemical properties of water change significantly as its temperature and pressure are raised. In particular, subcritical water shows pronounced properties of an acid–base catalyst, and this important circumstance makes it possible to carry out hydrolysis in the absence of conventional catalysts, such as acids and alkalis [4–6].

The main cellulose conversion pathways in subcritical and supercritical water were determined in earlier studies [3, 7–12]. Cellulose crystal structure disruption yielding soluble oligomers and oligomer fragmentation occur in sc-H_2O at a high rate, and so do secondary glucose conversions, such as dehydration, isomerization, and retro-aldol condensation. As a consequence, glucose conversion in sc-H_2O usually yields a multicomponent mixture of oligo- and monosaccharides and furfural derivatives [3, 9].

For selective synthesis of the most valuable products, namely, non-macromolecular sugars, it is pertinent to hydrolyze soluble polymers or oligomers at lower temperatures, using subcritical water. In order to optimize the process conditions—as will be demonstrated below, not only the reaction temperature, but also the reaction time needs optimization—it is necessary to have kinetic data for the process. Determination of kinetic parameters of the hydrolysis reactions in sc-H_2O is usually based on measuring the variation of the substrate weight or the total amount of carbon in cellulose and glucose oligomers [11, 12]. This circumstance makes it fairly difficult to compare the reactivities of non-macromolecular, oligomeric, and polymeric carbohydrates. As a consequence, it is difficult to optimize the reaction conditions for obtaining valuable products. Depending on the degree of polymerization, the same total mass of reacting carbohydrates may contain different numbers of key reaction sites, specifically, glycosidic ether linkages.

Here, we report a comparative estimate of the reactivities of the polymeric substrate and products of its hydrolysis in subcritical water. This estimate is based on the changes in the molar mass of the polymer subjected to hydrothermal treatment. However, it is technically difficult to directly monitor cellulose conversion in sc-H_2O, because cellulose is insoluble in water. For this reason, we studied the conversion of model substrates, namely, the water soluble sodium salt of carboxymethyl cellulose (CMC) and mono- and disaccharides (glucose, fructose, and sucrose).

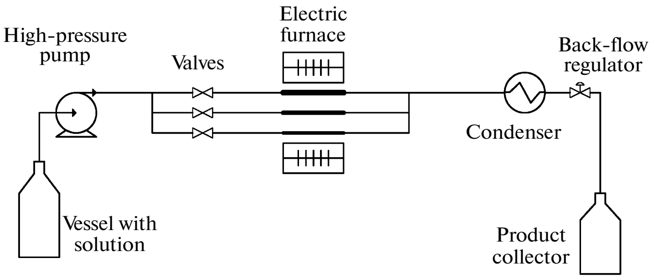

Fig. 1. Experimental setup for investigation of ply- and monosaccharide hydrolysis in subcritical and supercritical water.

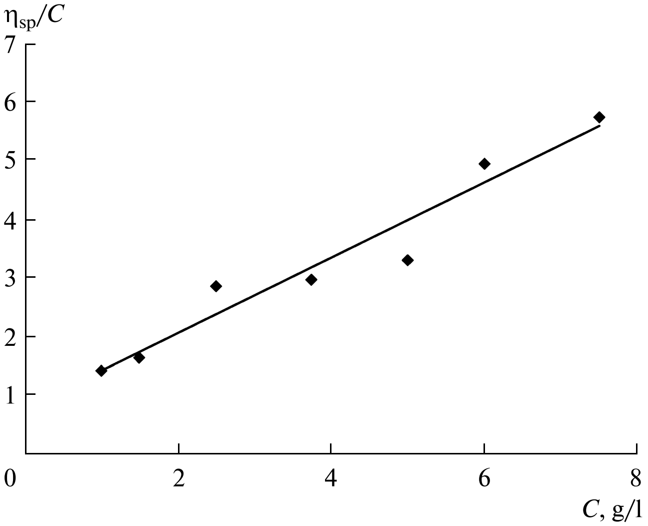

Fig. 2. Characteristic viscosity η_{sp}/C as a function of the CMC concentration in the solution.

EXPERIMENTAL

The conversions of glucose and fructose under subcritical conditions were studied in aqueous solutions at a monosaccharide concentration of 20 g/l, and the conversions of disaccharides and polysaccharides were studied using solutions of sucrose (20 g/l) and CMC (15 g/l).

The process was carried out using the laboratory setup schematized in Fig. 1. The setup can include several reactors with a volume of V_r = 0.11–4.4 ml. The reactor temperature was controlled with a Miniterm 400.31 regulator with an accuracy of ±2.0°C. The liquid reactants were fed into the system at a high pressure with a Gilson 307 pump, which is employed in high-performance liquid chromatography (HPLC). A pressure of up to 220 atm at the reactor outlet was maintained using a Tescom back-pressure regulator. The solution feed flow rate (v) was 1.0 ml/min. Since the solution flow was laminar (Re < 1000), it was possible to use the plug-flow reactor model in the kinetic description of the reaction.

The glucose, fructose, and sucrose concentrations in the reaction mixture were determined by HPLC on an Agilent 1100 chromatograph (Kromasil 100 Å 5 μm NH_2 column, acetonitrile : water = 70 : 30 mobile phase, 190 nm UV detector).

The changes in the molar mass as a result of CMC hydrolysis at 35 ± 0.1°C was estimated by measuring the viscosity of solutions at different CMC concentrations by capillary viscometry on a VPZh-4 viscometer with a capillary 0.62 mm in diameter. The solvent flow time was at least 100 s, and this obviated the need to apply kinetic energy corrections [13]. The flow time in each case was measured at least five times, and the discrepancy between measurements did not exceed 0.2–0.3 s. Reduced viscosity η_{sp}/C was determined as

$$\eta_{sp}/C = \frac{t_f/t_0 - 1}{C}, \qquad (1)$$

where t_f is the CMC solution flow time, t_0 is the solvent flow time, and C is the CMC concentration in the solution. Characteristic viscosity $[\eta]$ was determined by extrapolating reduced viscosity to infinite dilution (Fig. 2):

$$[\eta] = \lim_{C \to 0}\left(\frac{\eta_{sp}}{C}\right). \qquad (2)$$

The viscosity-average molar mass M was calculated using the Kuhn–Mark–Houwink equation [14]:

$$[\eta] = KM^{\alpha}, \qquad (3)$$

where $[\eta]$ is characteristic viscosity (cm^3/g); K is a factor depending on the temperature, polymer nature, and solvent; and α is the constant characterizing the conformation of the macromolecule in the solution. For CMC, $K = 1.23 \times 10^{-2}$ ml/g and $\alpha = 0.91$ [15].

The density of subcritical water was calculated using the WaterSteamPro software package (http://www.wsp.ru).

Because the density of water decreases with increasing temperature, the reaction time τ depends not only on the reactor volume V_r and volumetric feed flow rate v, but also on the temperature and pressure P:

$$\tau = \frac{V_r \rho_T}{\rho_{25} v}, \qquad (4)$$

where ρ_{25} and ρ_T is the density of water at 25°C and at temperature T, respectively. For convenient comparison of experimental data, we used the quantity V_r/v. The rate constants of chemical reactions were calculated using τ values determined via formula (4).

RESULTS AND DISCUSSION

Hydrolysis of Carboxymethyl Cellulose

Figure 3 and Table 1 present experimental data characterizing the variation of the viscosity-average molar mass M of CMC in subcritical water.

The acid hydrolysis of the ether linkages in sucrose and starch, the latter consisting of glucose monomer units bonded by ether linkages, occurs as a first-order reaction with respect to the substrate [16, 17]. It can, therefore, be assumed that the hydrolysis of CMC, which is a water-soluble ether of cellulose, is also a first-order reaction.

The viscometry technique employed in this study was used earlier in the kinetic study of cellulose ether conversion under mechanochemical treatment [18]. The variation of the molar mass of hydroxyethyl cellulose was fitted in that study to the first-order equation

$$\frac{\mathrm{d}(M_\infty - M)/M_\infty}{\mathrm{d}t} = \frac{k(M - M_\infty)}{M_\infty}, \qquad (5)$$

where M is the viscosity-average molar mass of the polymer at the point in time t, M_∞ is the limiting molar mass, and k is the rate constant of the reaction.

The CMC hydrolysis kinetics in subcritical water can be considered in the same way. This approach seems to be quite correct since one polymer molecule has a multitude of reaction sites, specifically, glycosidic linkages. It is most likely that the hydrolysis reactions of different macromolecules are independent of one another. Therefore, the rate of conversion of the polymeric substrate should be proportional not to the molecule concentration, but to the “concentration” of reaction sites in the polymer molecule, which is related to the molar mass of the polymer.

Equation (5) can be rewritten as

$$\frac{\mathrm{d}(M_1 - M)}{\mathrm{d}t} = k(M - M_1), \qquad (6)$$

where M is the viscosity-average molar mass of CMC at the point in time t and M_1 is the molar mass of the monomer unit of CMC. After integration of Eq. (6), the dependence of the molar mass of CMC in subcritical water on the reaction time will appear as

$$M = (M_0 - M_1)e^{-k\tau} + M_1, \qquad (7)$$

where M_0 is the molar mass of the initial CMC. To determine the rate constant, we will represent Eq. (7) in the following form:

$$k = \frac{1}{\tau}\ln\left(\frac{M_0 - M_1}{M - M_1}\right). \qquad (8)$$

The M_0 value derived from experimental viscosity data for the initial CMC (Fig. 2) using Eqs. (2) and (3) is 2.19×10^5 g/mol.

Table 1 lists the rate constants of CMC hydrolysis in subcritical water according to Eq. (8) under different experimental conditions (V_r/v and T).

From the temperature dependence of the rate constant of CMC hydrolysis (Table 1), we graphically derived the activation energy and preexponential factor: $E_a = 63.6$ kJ/mol and $\log A = 5.0$ [s^{-1}]. The calculated dependences of the molar mass M on the reaction temperature and time, derived using the above kinetic parameters, the Arrhenius equation, and Eq. (7), are plotted in Fig. 3.

According to the literature [3, 9, 19], the solution in which cellulose hydrolysis occurs at high temperatures may contain sugar decomposition products, such as furfural and 5-hydroxymethylfurfural. Upon CMC hydrolysis in subcritical water above 250°C at V_r/v = 264 and 50 s, the solution indeed acquires the brown color characteristic of furfural derivatives. For this reason, in order to optimize the process parameters for obtaining valuable products with high selectivity, it is necessary to compare the reactivities of CMC and the mono- and disaccharides under similar experimental conditions.

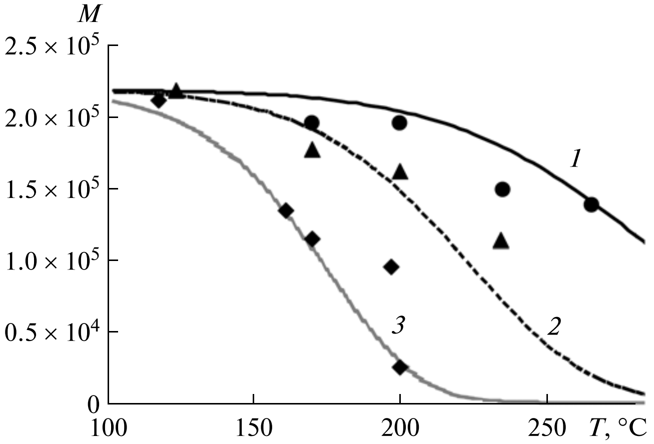

Fig. 3. Molar mass of CMC as a function of temperature at V_r/v = (*1*) 9, (*2*) (50), and (*3*) 264 s. The points represent experimental data, and the curves represent calculated data.

Conversions of Sucrose, Glucose, and Fructose

Tables 2–4 list experimental data on sucrose, glucose, and fructose conversions in subcritical water at different temperatures.

Table 1. CMC conversion at various temperatures and V_r/v ratios

T,°C	V_r/v, s	$M \times 10^{-5}$, g/mol	k, s^{-1}
25		2.19	–
120	264	2.12	1.3×10^{-4}
161	264	1.35	2.0×10^{-3}
170	264	1.14	2.7×10^{-3}
197	264	0.95	3.6×10^{-3}
200	264	0.24	9.6×10^{-3}
124	50	2.19	–
170	50	1.77	4.6×10^{-3}
200	50	1.62	6.9×10^{-3}
234	50	1.14	1.6×10^{-2}
170	9	1.96	1.4×10^{-2}
200	9	1.95	1.5×10^{-2}
235	9	1.49	5.2×10^{-2}
265	9	1.38	6.6×10^{-2}

Table 2. Sucrose conversion in subcritical water at various temperatures

T,°C	ρ, kg/m^3	Concentration × 10^2, mol/l			k, s^{-1}
		sucrose	glucose	fructose	
215	856	4.5	1.4	1.1	0.048
225	844	3.1	3.2	2.6	0.117
235	831	2.4	3.3	2.8	0.166
245	817	0.8	5.2	4.4	0.371
255	803	0	5.9	5.3	–
265	787	0	4.6	3.7	–
280	762	0	4.5	3.4	–

* The initial sucrose concentration is 5.9 × 10^{-2} mol/l. Glucose and fructose are absent at the beginning of the reaction. $V_r/v = 6.6$ s; $P = 140$ atm.

Table 3. Glucose conversion in subcritical water at various temperatures

T,°C	ρ, kg/m^3	Concentration × 10^2, mol/l		k, s^{-1}
		glucose	fructose	
200	874	11.3	0	0.006
230	838	11.0	0	0.011
260	795	10.5	0.2	0.021
290	744	7.8	0.6	0.082
320	676	3.4	0.5	0.276

The initial glucose concentration is 0.117 mol/l. Fructose is absent at the beginning of the reaction. $V_r/v = 6.6$ s; $P = 140$ atm.

Table 4. Fructose conversion in subcritical water at various temperatures

T,°C	ρ, kg/m^3	Fructose concentration × 10^2, mol/l	k, s^{-1}
200	874	11.5	0.003
230	838	11.2	0.008
260	795	8.6	0.058
320	676	3.1	0.286

The initial fructose concentration is 0.117 mol/l; $V_r/v = 6.6$ s; $P = 140$ atm.

Table 5. Activation energies and preexponential factors for the CMC, sucrose, cellobiose, glucose, and fructose conversions in subcritical water

Substrate	T,°C	E_a, kJ/mol	log A [s^{-1}]
CMC	120–265	64	5.0
Sucrose	200–245	134	12.9
Cellobiose [13]	320–400	123	10.1
Glucose	200–320	89	7.0
Fructose	200–320	88	7.1

The main products of sucrose hydrolysis are glucose and fructose, whose concentrations pass through a maximum as the temperature is raised (Table 2). Complete sucrose decomposition is attained at 255°C, with the fructose yield 11% lower than the glucose yield. The inequality of the fructose and glucose yields in the hydrolysis of the disaccharide can be due to the further conversion of the monosaccharides, for fructose is more reactive than glucose, other conditions being equal. This is indicated by our data on glucose and fructose decomposition in subcritical water (Tables 3, 4). At 260°C, the glucose conversion is only ~10% (Table 3), while the fructose conversion under the same conditions is 26% (Table 4).

Since the kinetics of the di- and monosaccharide conversions in subcritical water, like the kinetics of the same processes in "ordinary" water [16, 20–23], can be described in terms of a first-order rate equation, the sucrose, glucose, and fructose conversion rate constants were determined using the equation

$$k = -1/\tau \ln C/C_0, \tag{9}$$

where C_0 is the initial substrate concentration, C is the outlet concentration of the substance, and τ is the reaction time. The sucrose, glucose, and fructose decomposition rate constants determined using this equation are presented in Table 2–4. As was demonstrated above, the sucrose conversion rate constant refers to the hydrolysis of the glycosidic linkage of sucrose. According to the literature, glucose and fructose decomposition in sc-H_2O is a complicated combination of reactions including dehydration, isomerization, and retro-aldol condensation [3, 10, 11]. The temperature dependences of the rates of these reactions in the Arrhenius coordinates are shown in Fig. 4. The activation energies and preexponential factors for these reactions are listed in Table 5.

The activation energies for the disaccharides sucrose (Table 5) and cellobiose [22] are similar. Different values of the apparent activation energy of conversion in subcritical water have been reported for fructose (158 kJ/mol [21] and 96 kJ/mol [23] and glucose (119 kJ/mol [20]).

Comparing the Reactivities of Poly-, Di-, and Monosaccharides

The purpose of this study was to estimate the reactivities of CMC and of the products of its hydrolysis in subcritical water and to optimize the process conditions (temperature and reaction time) for obtaining sugars. Because the kinetic equation (7) describes the decrease in the molar mass of CMC rather than the formation of glucose monomers and dimers, this comparison cannot be carried out by the conventional method, comparing the rate constants of reactions at a fixed temperature. Non-macromolecular sugars form only at the latest stages of polymer hydrolysis. Therefore, for optimizing the sugar synthesis conditions, it is necessary to determine the "polymer depolymerization time," τ_d, defined as the minimum reaction time required for CMC hydrolysis to non-macromolecular products at a given subcritical water temperature.

An analysis of kinetic equation suggests that τ_d can be determined as follows. Substituting the condition $M = 2M_1$ into Eq. (8), we obtain

$$\tau_d = \ln\left(\frac{M_0 - M_1}{M_1}\right)[k_{CMC}(T)]^{-1}, \qquad (10)$$

where $k_{CMC}(T)$ is the CMC hydrolysis rate constant at temperature T determined using the Arrhenius equation. The condition $M = 2M_1$ was chosen for the reason that, at $M = M_1$, which means "total depolymerization," τ in Eq. (7) tends to infinity.

The stability of the cellulose hydrolysis products can be estimated as the glucose, fructose, and sucrose conversion (α) at the reaction time τ_d. The necessity of this estimate is dictated by the high polydispersity of the polymer solutions and by the roughness of the $M = 2M_1$ condition.

Let us represent Eq. (9) as

$$\alpha = 1 - \frac{C}{C_0} = 1 - \exp[-\tau k_{sug}(T)], \qquad (11)$$

where $k_{sug}(T)$ is the rate constant of mono- and disaccharide conversion in subcritical water at temperature T, determined using the Arrhenius equation. Combining Eqs. (10) and (11) yields

$$\alpha = 1 - \exp\left[\ln\left(\frac{M_1}{M_0 - M_1}\right)k_{CMC}(T)^{-1}k_{sug}(T)\right]. \qquad (12)$$

Equation (12) describes the temperature dependence of the sugar conversion α in subcritical water at the reaction time equal to the CMC depolymerization time τ_d. The value of α is the upper estimate of the actual conversion of the CMC hydrolysis products.

Figure 5 plots the temperature dependences of the sugar conversions calculated via Eq. (12) using the Arrhenius equation and the kinetic parameters of CMC, glucose, fructose, and sucrose hydrolysis (Table 5) at the reaction time equal to τ_d. The α values increase with increasing temperature (Fig. 5). At low temperatures of 100–115°C, the conversion of sucrose, a model dimer, is low ($\alpha < 0.15$). Evidently, under the CMC hydrothermal conversion in this temperature range, as well as at reaction times shorter than τ_d, it is possible to obtain products of partial CMC hydrolysis, namely, dimers and trimers.

Between 165 and 190°C, the sucrose conversion is close to unity and the glucose conversion is comparatively low ($\alpha < 0.6$). These temperatures are favorable for obtaining the monosaccharides. The data presented in Fig. 5 demonstrate that, by conducting CMC hydrolysis in subcritical water above 210°C, it is difficult to obtain non-macromolecular sugars in high yield and the reaction mixture is dominated by deep sugar decomposition products. This conclusion is in good agreement with the above experimental and literature data.

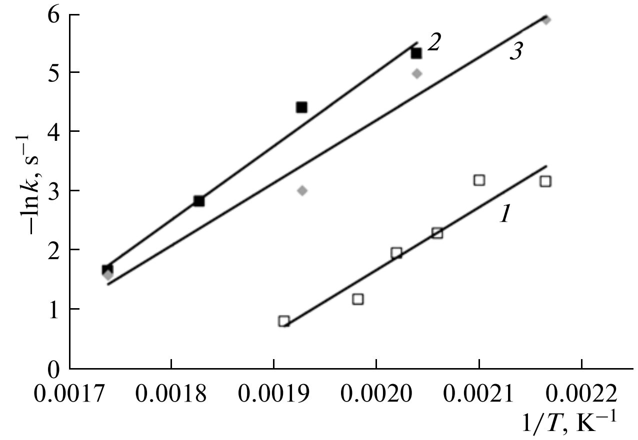

Fig. 4. Arrhenius plot of the rate constant of the conversion of (*1*) sucrose, (*2*) glucose, and (*3*) fructose.

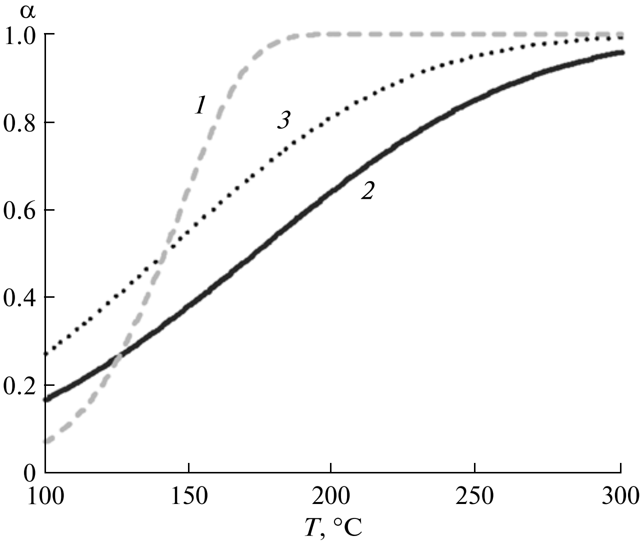

Fig. 5. (*1*) Sucrose, (*2*) glucose, and (*3*) fructose conversions as a function of temperature at the reaction time equal to the CMC depolymerization time at the corresponding temperature.

Thus, we have developed a kinetic model for CMC hydrolysis in subcritical water. The dependence of the CMC molar mass on the hydrolysis time is satisfactorily described by a first-order kinetic equation. Rate constants have been determined for CMC and sucrose hydrolysis and glucose and fructose conversions in subcritical water at different temperatures. The apparent activation energies of these reactions have been estimated. Sucrose hydrolysis in subcritical water can proceed selectively to yield monosaccharides throughout the temperature range examined. Kinetic data have been used to analyze the temperature effect on the qualitative composition of the CMC conversion products in subcritical water.

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