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Kinetic modeling of the multistep hydrolysis-dehydration of cellulose to platform molecules over a solid carbon acid catalyst in pure water

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Abstract

The present study was devoted to a kinetic modeling of cellulose hydrolysis-dehydration into platform molecules (glucose and 5-hydroxymethylfurfural) over a carbon solid acid catalyst. Cellulose depolymerization and transformations of the main process intermediates were experimentally studied under hydrothermal conditions in pure water over a catalyst based on sulfonated Sibunit material at 180 °C in a batch reactor. Based on the data obtained, the 18-step kinetic scheme of the process which included the main reaction pathways was proposed as well as the reaction constants were determined. Kinetic parameters showed that solid acid carbon catalysts seems to be more suitable than soluble ones for the production of 5-HMF from sugars. Proposed software modeling of cellulose hydrolysis-dehydration described the experimental results obtained with a sufficient accuracy.

Keywords

Cellulose, hydrolysis-dehydration, kinetics, modeling, Sibunit, carbon catalyst

Article Highlights

- Hydrolysis-dehydration of cellulose and process intermediates into glucose and 5-HMF platform molecules was studied
- Reactions were carried out over Sibunit carbon catalyst at 180 °C. 18-step kinetic model of the process was proposed
- Software modeling described the cellulose hydrolysis-dehydration with a sufficient accuracy

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Conflict of interest

The authors declare that they have no conflict of interest.

Availability of data and material (data transparency)

Not applicable

Code availability

Not applicable

1. Introduction

In the recent years research efforts have been focused on cellulose as a promising alternative raw material for chemical and fuel industries. Unlike oil, gas and coal traditional recourses, cellulose has a lot of advantages which are renewability, availability, comparatively low cost, as well as an absence of competition with the food industry for land and other resources [1-5]. The cellulose resources may be agricultural and wood processing wastes. Hydrolytic cellulose processing is one of the most actual fields of *fine chemistry*. This method of cellulose transformation, itself or combined with other processes, for example oxidation [6-8] or reduction [8-11], is suitable for the synthesis of valuable chemicals and non-petroleum fuels [2,12,13]. Cellulose hydrolysis-dehydration can be applied in the production of platform compounds: glucose, 5-hydroxymethylfurfural (5-HMF) and levulinic acid [2,5,8,12,14]. The process proceeds efficiently in the presence of solid acid catalysts such as metal oxides [15], nanodisperse metals [16], resins [15], and modified carbon materials [17]. Recently we reported solid acid catalysts based on Sibunit carbon material which demonstrated high activity in hydrolysis-dehydration of cellulose to glucose and 5-HMF [18].

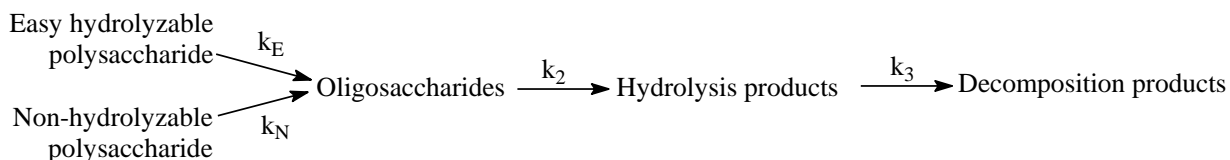
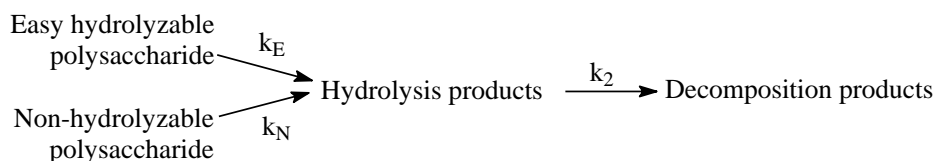
Research facilities in the field of cellulose hydrolysis-dehydration are not only aimed at the search for promising catalysts, process conditions and significant yields of the target products, but also search process mechanisms and kinetic parameters [1]. The kinetic studies and modeling of cellulose depolymerization into various chemicals are not trivial task. Cellulose hydrolysis-dehydration is a complex multistep process. It proceeds through a lot of pathways and a large number of intermediates can be formed [19]. Nevertheless, the simplest two-stage model of cellulose depolymerization was suggested in 1945 [20]. It included the cellulose conversion to the target products at the first stage and the decomposition of the target product at the second stage [21-29]:



Abatzoglou and co-authors reported a more complex kinetic model which involved separate stages of polysaccharide transformation into water-soluble oligosaccharides, their hydrolysis and the decomposition of the target products [30-32]:



Some other models reported previously took into account amorphous and crystalline domains in cellulose structure which were respectively easy and hard to hydrolyze [1,24,33,34]:



Kinetic equations of these models are used for calculating reaction constants, activations energies of stages and pre-exponential factors of kinetic constants. When modeling kinetics, all reactions involved are usually considered as irreversible and first order [20,33]. However, each kinetic model can be additionally modified for the observed experimental kinetic curves to be described more accurate. In particular, some stages can be regarded as reversible [30,35], as well as side reactions of cellulose hydrolysis-dehydration can be included [14]. Conner and co-authors suggested a model of cellulose hydrolysis-dehydration which involved two reversible transformations of glucose into disaccharides and anhydrosugars [36]. Bahari et al. found kinetic parameters of β -glucosane and mannoprotein conversions to 5-HMF [37]. Polysaccharide transformation scheme included five first-order stages [37]. Cantero et al. studied the fast cellulose hydrolysis-dehydration in supercritical water to determine kinetic parameters and activation energies. The kinetic scheme was rather complex but they did not report the kinetic modeling of the process [38]. Murzin and co-authors studied transformations of arabinogalactan polysaccharide using a scheme consisted of complex zero-order interconversions of the process intermediates. The kinetic scheme described the

formation of furfural and 5-HMF as the major products via the formation of soluble oligosaccharides followed by their hydrolysis-dehydration. Several other routes of intermediate and target product transformations were also taken into consideration. The scheme was treated using a special software.

The knowledge on the mechanism and kinetic regularities are certainly helpful for better understanding of the cellulose hydrolysis-dehydration and for predicting the optimal process conditions. Kinetic investigations are useful for scaling-up the laboratory process to industry. The kinetic schemes of the production of glucose and/or 5-HMF from cellulose reported elsewhere are usually based on simple kinetic models and involve only the main products and several process stages [21-23,31,39]. More complex kinetic schemes are rarely used because of the necessity of special software applications. The present study was focused on software modeling of the kinetics involving 18 stages of the cellulose hydrolysis-dehydration carried out over a solid acid catalyst based on **sulfonated** carbon material Sibunit.

2. Experimental

2.1 Chemicals

5-HMF (Sigma-Aldrich), D-fructose (Sigma-Aldrich), D-mannose (Sigma-Aldrich), D-glucose (Reahim, Moscow, Russia), D-cellobiose (Alfa Aesar), levulinic acid (Acros Organics) were purchased and used as HPLC standards. Milli-Q water (Millipore, France) was used for all experiments. Microcrystalline pure cellulose (Vekton, Saint-Petersburg, Russia) was mechanically activated before all the experiments. The polysaccharide was milled in a discrete action planetary mill Pulverizette 5 (Fristch, Germany) as we described previously [18]. **The crystallinity of the activated sample revealed by XRD (BrukerD8 Advabced, Germany) was 37%. The measurements of crystallinity are described in detail in the Supporting Information (SI) and our previous work [40]. The particle size measured by optical microscopy (Zeiss - Axiostar plus microscope equipped**

with a photcamera, Germany) was equal to $13\pm6\text{ }\mu\text{m}$. The average diameter of cellulose particles was calculated as the mean diameters of 100 particles.

2.2 Preparation of Sibunit carbon acid catalyst

The catalyst was prepared from mesoporous graphite-like carbon material (commercial name Sibunit, Omsk, Russia) via sulfonation in fuming H_2SO_4 as we reported previously [18]. Before preparing the catalyst, the carbon material was washed several times with boiling Milli-Q water. Then Sibunit was grinded and sifted through several sieves. The fraction of 560-940 μm was collected and washed again several times with boiling Milli-Q water. The typical procedure for preparing catalyst was the following. 1 g. of the grinded carbon was placed into a glass vessel. 15 mL of fuming H_2SO_4 was added. The vessel was heated upto 200 °C. The sulfonation time was 10 h. When the treatment was finished, the flask was cooled down. The catalysts was separated from the sulfuric acid, washed with boiling Milli-Q water and air-dried [18]. The catalyst was characterized by TEM, XRF, N_2 adsorption and acid-base titration with NaOH [18]. From TEM and low-temperature N_2 adsorption data, the carbon catalyst consisted of spherical carbon globules with the specific surface area of $400\text{ m}^2\cdot\text{g}^{-1}$. The catalyst surface acidity equal to $0.40\text{ mmol}\cdot\text{g}^{-1}$ was determined by acid-base titration. Before any catalytic experiment the catalyst was treated under hydrothermal conditions to remove weakly fixed acidic groups. Analysis of the treated catalyst by XRF revealed high stability of the sulfur content in the catalyst at the temperature up to 200 °C [18].

2.3 Catalytic tests

Hydrolysis-dehydration of cellulose over the Sibunit carbon catalyst was studied in a batch hastelloy autoclave (Autoclave Engineers, USA) at 180 °C, 1 MPa of Ar, under 1500 rpm stirring. The scheme of the experimental setup is shown in **Fig. 1**. Cellulose, catalyst and deionized Milli-Q water were placed into the reactor. Both the catalyst and cellulose concentrations were $10\text{ g}\cdot\text{L}^{-1}$. The volume of the reaction mixture was 45 mL. The autoclave was closed, the air was replaced with

argon. The reactor was heated to 180 °C, whereupon the reaction was started. Aliquots (~1 mL) of the reaction mixture were drawn from the reactor in 0, 1, 2, 3, 5 and 7 hours for HPLC analysis [18].

The transformations of cellulose hydrolysis-dehydration intermediates (cellobiose, glucose, fructose, 5-HMF, etc.) were also studied. Experiments in the batch reactor were carried out in the same way as cellulose transformation.

Aliquots of the reaction mixtures were analyzed by HPLC Shimadzu Prominence LC-20 (Japan) setup equipped with Rezex ROA-Organic Acids (Phenomenex, 300 mm·5.0 mm) column thermostated at 40 °C and **refractive index and diode array detectors**. The eluent was 1.25 mM H₂SO₄, the flow rate was 0.6 mL min⁻¹.

Product yields (Y) were calculated according to the formula (1):

$$Y = \frac{C_{\text{Product}} \cdot V}{N \times \left(\frac{m_{\text{cellulose}}}{M_{\text{glucan}}} \right)} \times 100, \quad (1)$$

where Y was a yield (%), C_{Product} (mol L⁻¹) was the concentration of a product, V was the solution volume (L), N was a **stoichiometric coefficient between a glucan unit and a product** (1 for glucose and 5-HMF, 6 for formic acid etc.), $m_{\text{cellulose}}$ was the mass of cellulose loaded to the reactor (g), and M_{glucan} was the molar mass of a glucan unit in cellulose (162 g·mol⁻¹).

To evaluate cellulose consumption, the reaction was carried out without drawing down any aliquots during 1, 2, etc. hours. The solids were separated from the reaction mixture by centrifugation, dried and weighted.

Cellulose consumption was calculated as following (2):

$$X = \frac{m_0 - m}{m_0}, \quad (2)$$

where X was cellulose consumption (%), m and m_0 were masses of cellulose (g) after and before the reaction, respectively.

3. Results and Discussion

3.1 Hydrolysis-dehydration of cellulose and main process intermediates

Cellulose hydrolysis-dehydration was experimentally studied using a batch reactor at 180 °C under inert atmosphere (argon pressure was 1 MPa) in the presence of a solid acid carbon catalyst. HPLC was used for analysis of the reaction mixture (**Fig. 2 a**). The maximal yield of glucose (45.9 %) was achieved in 2 h of the reaction. The maximal yield of 5-HMF was 18 % (5 h reaction time). It is mentioned above that cellulose transformation is a complex multistep process involving a large number of stages and intermediates [41]. In studying the complex chemical system, it is important to determine the basic process mechanism and all the reaction pathways, to identify intermediates and rate-determining stages. To model the cellulose hydrolysis-dehydration process, we proposed the kinetic scheme that took into account all the intermediates detected as well as the reactions between them (**Scheme 1**).

Main stages of the cellulose **hydrolysis-dehydration** process were separately studied. Experiments where intermediates were substrates were carried out over the carbon catalyst in the batch autoclave. The process conditions were the same as ones for cellulose transformation (180 °C, 1 MPa of Ar). Hydrolysis-dehydration of cellobiose, isomerization-dehydration of glucose, fructose and mannose, degradation of furfural and 5-HMF were separately investigated. **The experimental data obtained are presented in Fig. 2 and Fig. S1.** Hydrolysis-dehydration of cellobiose disaccharide made possible to determine the initial rate of hydrolysis of the β -(1-4)-glycosidic bond. Quick consumption of cellobiose was established (**Fig. S1 a**). The conversion of the disaccharide achieved 55 % at the beginning of the reaction. Cellobiose was spent completely in 0.5 h. This confirmed that the hydrolysis was a very fast reaction, and the overall kinetics of the cellulose hydrolysis-dehydration was limited by the cellulose depolymerization and formation of water-soluble oligosaccharides. Cellobiose hydrolysis was revealed to be an irreversible process. The kinetic model fitted the experimental data when repolymerization constant was close to zero. The first order of the β -(1-4)-glycosidic bond hydrolysis used for calculations in our study agreed with

the investigations reported previously. Thus, Saeman showed that the reaction order of hydrolytic cellulose transformations was in the range of 0.7-1.3 [20]. Bobleter and Bonn reported the first order of the cellobiose hydrolysis to glucose [42]. Experimental data demonstrated that glucose consumption was much slower than fructose one. In case of glucose hydrolysis, fructose was practically not accumulated and converted rapidly to 5-HMF. The yield of 5-HMF achieved 33 % in the experiment where fructose was spent. This value was higher than the 5-HMF yield reached from glucose (16 %) (**Fig. 2 c and d**). The high yields of 5-HMF derived from fructose were reported previously [41,43]. In the experiment with fructose, 5-HMF accumulation stopped as soon as fructose was fully converted. Glucose transformation proceeded slower compared with fructose consumption and resulted in lower 5-HMF yield. This was the evidence that glucose isomerization to fructose was the limiting stage of the process while fructose dehydration to 5-HMF was a fast reaction (**Scheme 1**). The consumptions of glucose and fructose plotted in logarithmic coordinates had linear dependences on the process time (**Fig. S2**). The first reaction order of sugar conversions was reported elsewhere [20,44-46]. **According to the experimental data, mannose was formed from both glucose and fructose.** The experiment with 5-HMF as a substrate revealed low stability of the compound. The conversion of 5-HMF reached 70 % in 7 h (**Fig. 2 e**). The formation of sugars was not observed what confirmed that dehydration of fructose to 5-HMF was an irreversible reaction. On the other hand, levulinic and formic acids were not accumulated from 5-HMF in significant yields. These data confirmed the transformation of 5-HMF via alternative pathway of high-temperature polycondensation to give side products [47-49]. When fructose and 5-HMF were used as substrates (**Fig. 2 c and e**), furfural was demonstrated only to form from fructose but not from 5-HMF. Minor yields of furfural equal to 1–2 % were observed. **The kinetics of furfural transformation was also investigated (Fig. S1 b).** Compared to 5-HMF, furfural demonstrated better stability under reaction conditions. Negligible yield of formic acid from furfural was detected, accumulation of sugars was not observed.

3.2 Kinetic modeling of the cellulose hydrolysis-dehydration

All the identified intermediates and products were added to the scheme of the reaction (**Scheme 1**). The constants of the reactions and chemical interactions were revealed from the experimental kinetic curves (**Table 1**). The kinetic modeling was based on the following assumptions. The first orders of all the stages were assumed as consumptions of all the intermediates had a linear dependence in $\ln(C/C_0)$ vs time coordinates (**Fig. S2**). The rates of proton adsorption/desorption during cellulose dissolution in water and the diffusion rates to the surface of the Sibunit solid catalyst were high enough and the reaction constants revealed were of chemical interactions but not of diffusion.

Based on the experimental data (**Scheme 1**), a following system of differential equations was proposed for modeling the kinetic curves.

$$\begin{aligned}
 \text{(I)} \quad & \frac{d}{dt} X(t) = -k_0 \cdot (1 - X(t)) , \\
 \text{(II)} \quad & \frac{d}{dt} \text{Olig}(t) = k_0 \cdot (1 - X)(t) - k_1 \cdot \text{Olig}(t) , \\
 \text{(III)} \quad & \frac{d}{dt} \text{Cellb}(t) = k_1 \cdot \text{Olig}(t) - k_2 \cdot \text{Cellb}(t) , \\
 \text{(IV)} \quad & \frac{d}{dt} \text{Glu}(t) = k_2 \cdot \text{Cellb}(t) + k_{31} \cdot \text{Fru}(t) + k_{43} \cdot \text{Mann}(t) - (k_3 + k_{34} + k_{30}) \cdot \text{Glu}(t) , \\
 \text{(V)} \quad & \frac{d}{dt} \text{Fru}(t) = k_3 \cdot \text{Glu}(t) + k_{41} \cdot \text{Man}(t) - (k_{31} + k_4 + k_5 + k_6 + k_{50}) \cdot \text{Fru}(t) , \\
 \text{(VI)} \quad & \frac{d}{dt} \text{Man}(t) = k_4 \cdot \text{Fru}(t) + k_{34} \cdot \text{Glu}(t) - (k_{41} + k_{43} + k_{40}) \cdot \text{Man}(t) , \\
 \text{(VII)} \quad & \frac{d}{dt} 5 - \text{HMF}(t) = k_5 \cdot \text{Fru}(t) - (k_7 + k_8) \cdot 5 - \text{HMF}(t) , \\
 \text{(VIII)} \quad & \frac{d}{dt} \text{Furf}(t) = k_6 \cdot \text{Fru}(t) - (k_9 + k_{11}) \cdot \text{Furf}(t) , \\
 \text{(IX)} \quad & \frac{d}{dt} \text{LA}(t) = k_7 \cdot 5 - \text{HMF}(t) - k_{12} \cdot \text{LA}(t) , \\
 \text{(X)} \quad & \frac{d}{dt} \text{FA}(t) = k_7 \cdot 5 - \text{HMF}(t) + k_9 \cdot \text{Furf}(t) - k_{10} \cdot \text{FA}(t) ,
 \end{aligned}$$

where Cellb was Cellobiose, Glu was Glucose, Fru was Fructose, Man was Mannose, Furf – Furfural, LA was Levulinic acid, FA was Formic acid. X was a cellulose conversion applied instead of cellulose concentration. X value was used as cellulose was a insoluble compound [20,50].

The constant k_0 of cellulose dissolution determined from the cellulose consumption measured according to the formula (2) was equal to $16 \cdot 10^{-3} \text{ min}^{-1}$. The constant meaning was low enough compared to k_2 determined experimentally from cellobiose transformations (0.11 min^{-1}). This indicated that cellulose transformation to water soluble oligosaccharides but not hydrolysis itself was a limiting stage of cellulose processing. When modeling cellulose hydrolysis-dehydration the value of k_1 of water-soluble oligomer hydrolysis was assumed to be equal to k_2 as both constants described the cleavage of the β -(1-4)-glycosidic bond (**Scheme 1**). Hydrolysis constant was more than other constants by an order of magnitude. Hence, hydrolysis proceeded at a very high rate. The revealed constant k_3 of isomerization of glucose to fructose was lower than the observed constant k_5 of fructose dehydration to 5-HMF by a factor of 2.4. That demonstrated glucose consumption to fructose was limited by isomerization to result in a decrease in the yield of 5-HMF. Constants k_3 determined from kinetic experiments with glucose as a substrate was $8.0 \cdot 10^{-3}$. The value of k_{31} was evaluated from thermodynamic data. According to Tewari and Goldberg, equilibrium constant for glucose-fructose isomerization at 180°C is 2.6 [51]. This came to $k_{31}=k_3/K=8.0 \cdot 10^{-3}/2.6=3.07 \cdot 10^{-3} \text{ min}^{-1}$. Delidovich and co-authors reported that a certain combination of the equilibrium constants for the interconversions of monosaccharides was equal to 1 [52]. Thus, $\frac{k_3 \cdot k_4 \cdot k_{43}}{k_{31} \cdot k_{34} \cdot k_{41}} = 1$ equation gave k_4 value of $7.4 \cdot 10^{-3} \text{ min}^{-1}$.

When modeling the cellulose hydrolysis-dehydration additional degradation of glucose, fructose and mannose monosaccharides was presumed via pathways with rate constants k_{30} , k_{50} and k_{40} , respectively. Contradictory data on an existence of these side transformations were shown previously. Thus, fructose transformation to glyceraldehydes and then to pyruvaldehyde and lactic acid was revealed by some researchers [38,45,48,53,54]. On the other hand, some doubt of the occurrence of these routes in the presence of an acid catalyst at temperatures below 270°C was stated [47]. Similar to fructose, dehydration of glucose to 1,6-anhydroglucose [45,48] as well as cleavage of glucose to erythrose could take place [45,49,53]. The modeling made in the present

work confirmed the existence of fructose and glucose decomposition to side products. Thus, when the value of k_{50} was equated with zero kinetic modeling of hydrolysis-dehydration of cellulose, as well as calculations on the other sugars gave higher yields of 5-HMF against the experimental data (**Fig. S3**). The constants of sugar consumption k_{30} , k_{40} and k_{50} were determined from the available experimental and **thermodynamic** data via subtraction of constant values of monosaccharide transformations via confirmed pathways from the constant values of glucose, fructose and mannose total consumption, for example $k_{30} = k_{\text{Glu}} - k_3 - k_{34}$.

The experimental data presented in this work demonstrated the difference of the catalytic action between the solid Sibunit carbon and soluble sulfuric acid catalysts in cellulose hydrolysis-dehydration. As stated above, the kinetic investigations were carried out at 180 °C and pH value of 2.7 in this work. The determined constant k_2 (0.11 min^{-1}) of cellobiose hydrolysis to glucose over solid acid carbon catalyst was lower by a factor of 3.2 than the value observed previously in the presence of H_2SO_4 (pH 2.1, 180 °C) [55]. The total constant of glucose consumption through various pathways k_{glu} ($10.6 \cdot 10^{-3} \text{ min}^{-1}$) was higher than the value revealed previously in the presence of H_2SO_4 at pH of 2.1 and 180 °C [55]. J. F. Saeman reported the glucose degradation constant equal to $24.1 \cdot 10^{-3}$ under 180 °C but pH value of ca. 1.1 [20]. The reaction constant k_7 of 5-HMF hydration into levulinic and formic acids was in 25 times lower than the constant of 5-HMF degradation to side compounds ($k_8 = 5.1 \cdot 10^{-3} \text{ min}^{-1}$). This can explain why the formation of levulinic acid is not significant over solid carbons while it is easily produced in the presence of soluble acid catalysts under close conditions (temperature and pH) [18,56-58]. Thus, the data demonstrated that solid acid catalysts seems to be more suitable than soluble ones for the production of 5-HMF from the polysaccharides.

The system of differential equations was solved by the Mathcad 15.0 software with function Odesolve based on the Runge–Kutta method with an automatic step-size for solving. The developed kinetic model provided not only qualitative but also accurate enough quantitative description of cellulose hydrolysis-dehydration, as well as transformations of intermediates of the process under

study (**Fig. 2**). It should be noted that the proposed model is applicable not only in the case of using cellulose as a substrate. Modeled kinetics also describes accurately the experiments where other intermediates glucose, fructose, mannose, and 5-HMF are substrates (**Fig. 2**).

Conclusions

The kinetic model which consisted of eighteen stages was proposed to predict cellulose hydrolysis-dehydration over a solid sulfonated Sibunit carbon catalyst in a batch reactor. The model described in the paper was based on the experimental data on hydrolysis-dehydration of cellulose the main process intermediates (cellobiose, glucose, fructose, mannose, 5-HMF, furfural, levulinic acid). Kinetic parameters of the reactions were revealed. Cellulose depolymerization was established to be limiting stage of cellulose processing, while hydrolysis of β -(1-4)-glycosidic bond in cellulose and oligosaccharides was a fast reaction. The difference of the catalytic action between the solid carbon and soluble acid catalysts in cellulose hydrolysis-dehydration was demonstrated. The degradation of 5-HMF into levulinic acid is not significant over solid carbons while it is the main reaction way in the presence of soluble acid catalysts under close conditions. Thus, solid acid carbon catalysts seems to be more suitable than soluble ones for the production of 5-HMF from sugars. The data on side conversions of monosaccharides were specified. The kinetic model of cellulose hydrolysis-dehydration was updated by adding side reactions of sugar decomposition and glucose conversion to mannose. A system of differential equations was solved using the Mathcad software. The computational model described well the chemical experimental data observed.

1 **Table 1.** Constants of the cellulose hydrolysis-dehydration reactions

Constant	Interaction	Constant values, min ⁻¹		
		This work ^[a]	Described in literature	
			value	Ref.
k ₀	cellulose dissolution	16·10 ⁻³		
k ₁	Oligosaccharide hydrolysis	0.11		
k ₂	hydrolysis of cellobiose to glucose	0.11	0.356	[55] ^[b]
k _{glu}	the constant of glucose consumption via all the pathways	10.6·10 ⁻³	4.4·10 ⁻³	[55] ^[b]
			3.0·10 ⁻³	[46] ^[c]
			12.1·10 ⁻³	[46] ^[d]
			0.225	[28] ^[e]
			24.1·10 ⁻³	[20] ^[f]
k ₃	isomerization of glucose to fructose	8.0·10 ⁻³		
k ₃₁	izomerization of fructose to glucose	3.07·10 ⁻³		
k ₃₀	degradation of glucose to side products	0.5·10 ⁻³		
k _{man}	the constant of mannose consumption via all the pathways	7.22·10 ⁻³	7·10 ⁻³	[46] ^[g]
			18·10 ⁻³	[46] ^[h]
k ₃₄	isomerization of glucose to mannose	1.6·10 ⁻³		
k ₄₃	isomerization of mannose to glucose	0.4·10 ⁻³		
k ₄₀	degradation of mannose to side products	2.0·10 ⁻³		
k _{fru}	the constant of fructose consumption via all the pathways	4.37·10 ⁻²		
k ₄	isomerization of fructose to mannose	7.4·10 ⁻³		

k ₄₁	isomerization of mannose to fructose	$4.82 \cdot 10^{-3}$		
k ₅₀	degradation of fructose to side products	$11.5 \cdot 10^{-3}$		
k ₅	dehydration of fructose to 5-HMF	$1.95 \cdot 10^{-2}$		
k ₆	dehydration of fructose to furfural	$2.23 \cdot 10^{-3}$		
k _{5HMF}	the constant of 5-HMF consumption via all the pathways	$5.3 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	[46] ^[i]
			$6 \cdot 10^{-3}$	[46] ^[k]
k ₇	hydration of 5-HMF to levulinic and formic acids	$0.2 \cdot 10^{-3}$		
k ₈	degradation of 5-HMF to side products	$5.1 \cdot 10^{-3}$		
k ₉	hydration of furfural to formic and 4-hydrobutyric acids	$2.3 \cdot 10^{-3}$		
k ₁₀	degradation of formic acid to side products	$1.7 \cdot 10^{-3}$		
k ₁₁	degradation of furfural to side products	$2.1 \cdot 10^{-3}$		
k ₁₂	degradation of levulinic acid to side products	$1 \cdot 10^{-4}$		

2 Reaction conditions: [a] any substrate 10 g·L⁻¹, Sibunit carbon catalyst 10 g·L⁻¹, reaction mixture volume 45 mL, 180 °C, Ar inert atmosphere 1
3 MPa; [b] cellobiose substrate 10 g·L⁻¹, H₂SO₄ catalyst, pH 2.1, 180 °C; [c] glucose substrate 1 g·L⁻¹, H₂SO₄ catalyst, pH 2.5, 170 °C; [d] glucose
4 substrate 1 g·L⁻¹, H₂SO₄ catalyst, pH 2.5, 190 °C; [e] 1.288% H₂SO₄ catalyst, pH 0.85, 200 °C; [f] 0.8% H₂SO₄ catalyst, pH of ca. 1.1, 180 °C; [g]
5 mannose substrate 2 g·L⁻¹, H₂SO₄ catalyst, pH 2.5, 170 °C; [h] mannose substrate 2 g·L⁻¹, H₂SO₄ catalyst, pH 2.5, 190 °C; [i] 5-HMF substrate 3 g·L⁻¹,
6 H₂SO₄ catalyst, pH 2.5, 170 °C; [k] 5-HMF substrate 3 g·L⁻¹, H₂SO₄ catalyst, pH 2.5, 190 °C.

7

8

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