J Mater Sci (2008) 43:2179–2188
DOI 10.1007/s10853-007-2043-6

NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Liquefaction kinetics of cellulose treated by hot compressed water under variable temperature conditions

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Received: 13 November 2006 / Accepted: 20 July 2007 / Published online: 29 November 2007

Abstract In this study, we investigate a process for liquefaction of cellulose with hot compressed water as a pre-treatment for a compact gasification process of cellulose. Experiments were carried out using a batch reactor with a temperature controller. The temperature profile for heating was controlled in a proportional relationship with time. Cellulose was drastically decomposed and liquefied when the maximum temperature was set at over $\sim$513 K. It decomposed to oligosaccharides, monosaccharides and pyrolysis products such as glyceraldehydes and 5-hydroxymethyl-2-furaldehyde. Theoretical treatment was investigated by considering the following stepwise processes: decompositions of I. cellulose to oligosaccharides, II. oligosaccharides to monosaccharides and pyrolysis products and III. monosaccharides to pyrolysis products. In these steps, step I is a heterogeneous reaction consists of: (a) Diffusion of water monomer to a cellulose surface and (b) Hydrolysis reaction of water monomer with a cellulose molecule at the surface. The temperature dependence of the rate constants was expressed by the Arrhenius relationship. The calculated result showed good correlation to the experimental data. The results suggest that it is possible to estimate the decomposition of cellulose by hot compressed water in a batch reactor that requires slow heating process.

Nomenclature

C_b	Concentration of water monomer in the bulk (mol/m^3)
C_e	Concentration of chemicals after the reaction (mol/m^3)
C_i	Concentration of chemicals (mol/m^3)
C_s	Concentration of water monomer at the surface of cellulose particle (mol/m^3)
DP	Degree of polymerization
E_{ai}	Activation energy (kJ/mol)
R	Gas constant (J/(mol K))
T	Temperature (K)
T_{init}	Initial temperature (K)
T_{max}	Maximum temperature set as an experimental condition (K)
V	Volume of the reactor (m^3)
W_{A1}	Mass transfer rate of water monomer (mol/s)
W_{A2}	Hydrolysis reaction rate at the surface of a cellulose particle (mol/s)
h	Time interval set for the calculation of the fourth-order Runge-Kutta method (s)
k_{0i}	Frequency factor (−)
k_1	Apparent rate constant of cellulose decomposition (mol$^{1/3}$/(m s))
k_2	Rate constant of Eq. 5 (1/s)
k_3	Rate constant of Eq. 6 (1/s)
k_4	Rate constant of Eq. 7 (1/s)
k_c	Mass transfer coefficient of water monomer through the aqueous film surrounding a cellulose particle (m/s)

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k_s	First order rate constant of hydrolysis reaction for cellulose decomposition (m/s)
m_0	Loaded weight of cellulose particle (g)
r	Radial position of cellulose surface (m)
r_0	Radius of unreacted cellulose particle (m)
r_1	Reaction rate of elementary process shown as Eq. 4 (mol/(m^3 s))
r_2	Reaction rate of elementary process shown as Eq. 5 (mol/(m^3 s))
r_3	Reaction rate of elementary process shown as Eq. 6 (mol/(m^3 s))
r_4	Reaction rate of elementary process shown as Eq. 7 (mol/(m^3 s))
r_A	Apparent reaction rate of water monomer for unit cellulose particle (mol/s)
r_B	Apparent reaction rate of cellulose molecule for unit cellulose particle (mol/s)
r_{Cel}	Decomposition rate of cellulose particle (mol/(m^3 s))
$r_{Oligo,d2}$	Decomposition rate of oligosaccharides to monosaccharides (mol/(m^3 s))
$r_{Oligo,d4}$	Decomposition rate of oligosaccharides to pyrolysis products (mol/(m^3 s))
$r_{Pyro,f3}$	Formation rate of pyrolysis products from monosaccharides (mol/(m^3 s))
$r_{Pyro,f4}$	Formation rate of pyrolysis products from oligosaccharides (mol/(m^3 s))
r_i	Overall reaction rate of chemicals (mol/(m^3 s))
$r_{i,d}$	Total decomposition rate of chemicals (mol/(m^3 s))
$r_{i,f}$	Total formation rate of chemicals (mol/(m^3 s))
t	Time (s)
t_{Tmax}	Holding time of temperature at T_{max} [s]
v_T	Heating rate (K/s)
x	Decomposition ratio of unit cellulose particle (–)

Greek letters

ρ	Molar density of the cellulose particle (mol/m^3)

Subscripts

1∽4	Reaction described in Eqs. 4∽7
Cel	Cellulose molecule
Mono	Monosaccharides
Oligo	Oligosaccharides
Pyro	Pyrolysis products
d	Decomposition
f	Formation

Introduction

The development of an effective utilization process to deal with the energy problem from a lack of fossil fuels is desired austerely. Biomass is an important resource that can be converted to energy. Particularly, wood biomass is one of the most useful resources. Using supercritical, subcritical and hot compressed water for converting cellulose to valuable renewable resources for energy, chemicals, food and feedstock has been extensively examined [1–24]. The early studies, which were mainly carried out by Elliott and his colleagues, are summarized in the review presented by Sealock et al. [2]. Antal and his colleagues also carried out extensive work on supercritical, subcritical and hot compressed water conversion of biomass feedstock and biomass-related organics [3–7]. In their research, they reported that the lignin and hemicellulose undergo solvolysis when the temperature is above 463 K. They reported that large yields (>2×10^{-3} m^3/g) of gas with a high content of hydrogen (57 mol%) were realized using an appropriate catalyst and operating at high temperature. Minowa and his co-workers investigated the liquefaction and gasification of cellulose with hot compressed water and supercritical water [8–14]. They investigated the effect of temperature on cellulose decomposition and reported that cellulose decomposition was started below 473 K, became fast around 513–543 K, and complete decomposition was achieved at 553 K. Arai and his co-workers investigated cellulose reforming with subcritical and supercritical water [15–20]. They also investigated the gasification of lignin with supercritical water treatment [19, 21, 22].

In recent years, as well as fundamental studies being carried out, practical uses of the process have been developed. One of the proposed process is a compact process, which achieved by a so-called microreactor. The microreactor can achieve quick heating and rapid quenching of the reaction [17, 20, 25–29]. By using the microreactor, the aimed reaction can be rapidly and selectively promoted by setting the desired temperature and preferable residence time. In fact, a remarkable rapid decomposition of cellulose, of several seconds or less without using catalysis, was reported by Sasaki et al. [17]. A numbering-up of the device allows the rapid manufacturing in large quantities and the direct commercialization of laboratory experiments.

In recent years, we started to investigate the gasification of wood biomass based on the concept of the microreactor device. The final object of a series of studies was to achieve a rapid manufacturing process of hydrogen from Japanese cedar. Before examining the gasification of wood biomass, we faced a serious problem, i.e., the liquefaction of a solid sample of wood biomass. A solid sample having large particle diameter cannot be fed into the microreactor which has a narrow channel. If we use the microreactor for the treatment of solid material, it is necessary to liquefy it beforehand. Once the solid sample is liquefied, we can adopt a compact device for subsequent treatment. In this study, we examine the liquefaction of a solid sample by using a batch reactor in which large amount of wood biomass can be treated. In the actual process of liquefying a solid biomass by batch reactor, quick heating and rapid quenching are difficult to achieve. It is important to know the reaction profile in the batch reactor which accompanies the heating and quenching processes. The aim of this study is to estimate the reaction profile of solid cellulose as a model sample of wood biomass by using a batch reactor with temperature controller. The experiments are carried out at relatively low temperatures to provide formation of char products. The liquefaction profile of solid cellulose particles in hot compressed water is experimentally measured and theoretically predicted.

Experimental

Reagents

Cellulose used was de-ashed microcrystalline cellulose (Avicel No. 2331; average particle diameter 20–100 μm) purchased from Merck. The reagents used for High Performance Liquid Chromatography (HPLC) analysis are as follows: cellobiose (>99%), cellotriose (>98%), cellotetraose (>95%), cellopentaose (>95%), erythrose (50%), pyrvaldehyde (40%), glyceraldehyde (>95%), and 5-HMF (>99%) (Sigma-Aldrich Japan K.K. Co. Ltd. (Tokyo)); glucose (>99%), fructose (>99%) (Wako Pure Chemicals Industries Ltd. (Osaka)).

Cellulose liquefaction experiments and product analysis

The experiments were performed on a batch basis in a standard 97 cm^3 stirred reactor fabricated from HastelloyC-22 with four cartridge heaters. The schematic of the batch reactor system is presented in Fig. 1. The reactor equipped two type K thermocouples. One was set to measure the temperature of the inner aqueous phase of the reactor, while the other was to measure the temperature of the reactor wall in which the cartridge heaters were stuck. The thermocouples and the cartridge heaters were connected to the system controller. The temperature of the inner aqueous phase during the heating process was controlled by PDI control. The temperature was varied according to the temperature profile which was set by a computer program. The monitored temperatures were recorded in notebook PC. The reactor also equips a pressure indicator and N_2 line to purge the air. The system was also configured with pressure and temperature alarms, which turned off the furnace if the pressure or temperature exceeded preset limit. The batch system was also equipped with a gas sampling part. After the reaction, the produced gas sample was collected through a diaphragm pump. The obtained gas samples were analyzed with a gas chromatograph (GC) system (Shimadzu, GC-2014). Carbon dioxide and oxygen gas were detected when the maximum temperature was set over 533 K, but their quantities were extremely low (they were below 7×10^{-4} mol even when maximum temperature was set at 553 K). Therefore, in this study, the produced gas sample was neglected for data treatment.

The liquefaction experiment was carried out as follows. A 0.7 g of cellulose sample and 69.3 g of ultra pure water were introduced into the reactor cell. The reactor cell was attached to the system and sealed. The reactor was purged and pressurized with N_2 gas to 1 MPa. This high loading N_2 gas prevented evaporation of water. The reactor was checked for leaks. The stirrer was subsequently started, and the reactor and its contents were heated according to the pre-set temperature program. In this study, the heating rate of the aqueous medium was set at 0.1 K/s. The maximum temperatures were set at 443, 473, 503, 513, 523, 533, and 553 K. After the medium temperature reached the maximum temperature, the temperature was kept at maximum temperature for desired holding time. As soon as the holding time passed, heating was ceased and the reactor was subsequently cooled by air-cooling at room temperature. After the reactor contents were fully cooled, the reactor cell was separated from the system. The entire contents in the reactor cell were collected. The collection ratios were over 99% for all experiments. The collected sample was then filtrated through a PTFE membrane filter with a pore size of 0.5 μm. The solid residue was dried at room temperature in a vacuum desiccator, and weighed. The decomposition ratio of cellulose particle was calculated from the mass balance of the solid sample before and after reaction. The composition of the liquid filtrate was analyzed by HPLC (Shimadzu co. ltd.). The HPLC equipment consisted of an isocratic pump (LC-10ADvp), an autosampler (SIL-10ADvp), and a system controller (SCL-10Avp). The column used for the analysis was a Shim-pack SPR-Ca. The HPLC was operated at an oven temperature of 358 K, with a flow of the water solvent of 1.0×10^{-2} cm^3/s. The detector used was a refractive index detector (RID-10A). Peak identification was established by standard solution of the pure compound. Calibration of the peaks was performed using standard solutions of varying concentrations to develop a linear relationship between the peak areas and the corresponding concentrations.

Results and discussion

The HPLC chromatograms of the products at temperatures of 443, 473, 493, 513 and 533 K are shown in Fig. 2a. That of 523 K is also shown in Fig. 2b with the retention times

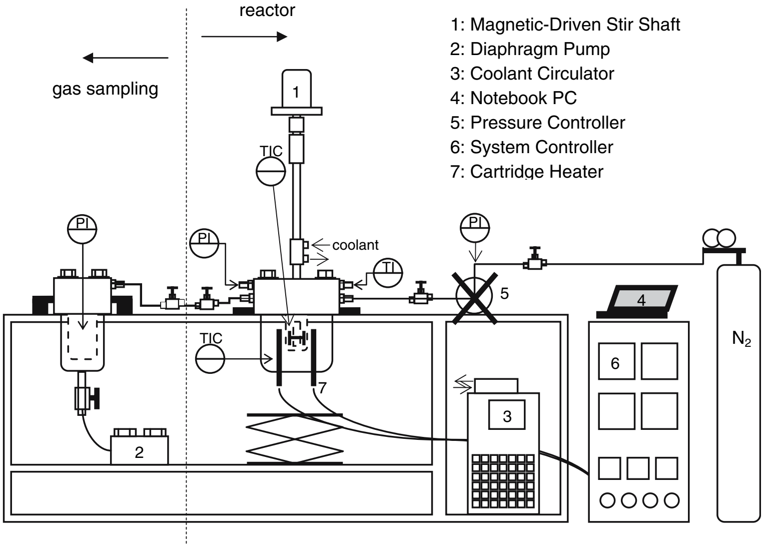

Fig. 1 Schematic of batch reactor system

of the pure chemicals, which are indicated by vertical broken lines. As shown in Fig. 2a, the concentration of glucose, fructose, glyceraldehyde, and 5-HMF increase by increasing the maximum temperature. Although it is hard to read from Fig. 2a, the concentration of oligosaccharides also depends on the maximum temperature. Figure 3 shows both concentration profiles for oligosaccharides and cellulose. As shown in Fig. 3, at 473 K as maximum temperature, the concentration of cellotetraose, cellotriose and cellobiose increased. At that maximum temperature, cellulose decomposition had started slightly. The cellotetraose concentration shows a maximal value at $T_{\max}$ 493 K. The maximal concentration of cellotriose is at 513 K. The concentration of cellobiose increased monotonically, and its maximal concentration was not detected $T_{\max} < 543$ K. The concentration of cellulose monotonically decreased above ~473 K. These results show that cellulose is decomposed to oligosaccharides, having a high degree of polymerization (*DP*), and the higher *DP*-oligosaccharides are decomposed to lower *DP*-oligosaccharides by degrees. Considering the results of Figs. 2 and 3 together, it is further suggested that lower *DP*-oligosaccharides are decomposed to monosaccharides and pyrolysis products. The suggested pathway of decomposition reaction supports the pathway as previously reported Sasaki et al. [17, 20], and also supports the assumption of the theoretical model which is proposed in this study.

Subsequently, we tried to estimate the experimental results by a theoretical calculation. We considered that the cellulose particle decomposes according to the following stepwise processes: 1. solid cellulose particle is hydrolyzed to oligosaccharides, 2. formed oligosaccharides decompose to both monosaccharides and pyrolysis products, 3. monosaccharides decompose to pyrolysis products, and 4.

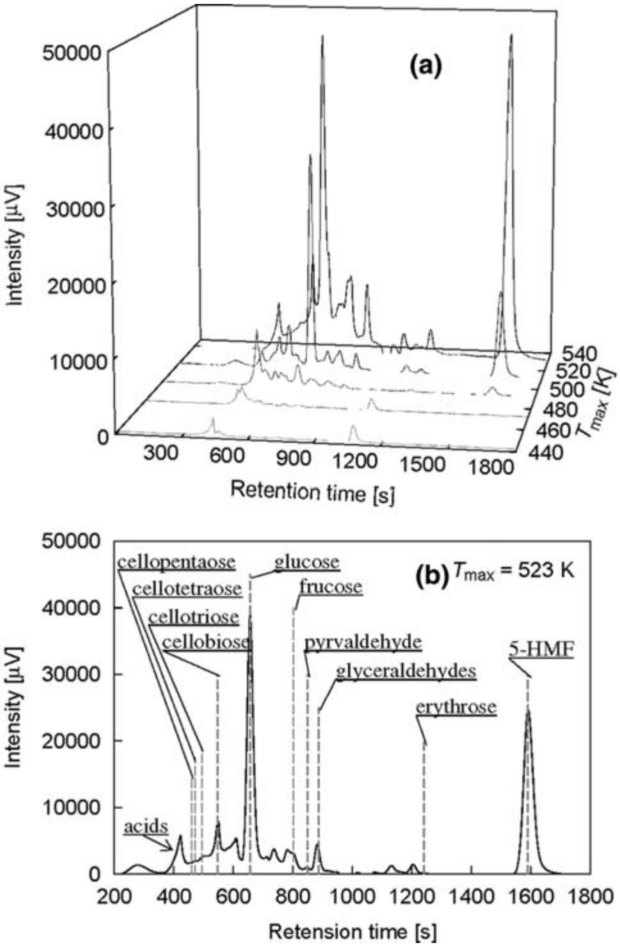

Fig. 2 HPLC chromatograms of recovered liquid samples. v_T 0.1 K/s, $t_{T\max}$ 0 s. (**a**) Results for several $T_{\max}$. (**b**) Result at $T_{\max}$ 523 K and retention times of pure chemicals

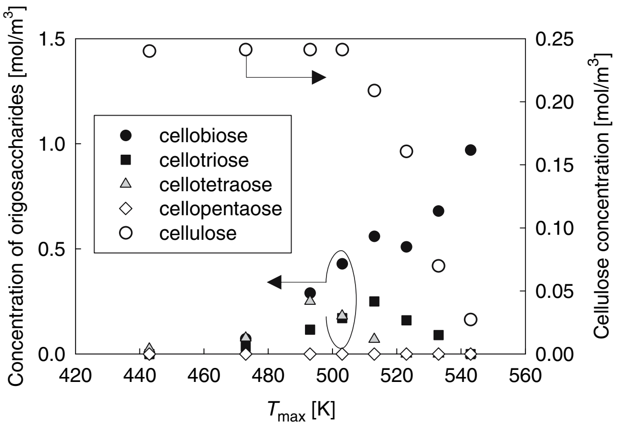

Fig. 3 Effect of T_{max} on cellulose and oligosaccharides concentrations. v_T 0.1 K/s, t_{Tmax} 0 s

pyrolysis products are polymerized and form tar or char products. This suggested reaction pathway for cellulose decomposition with hot compressed water is the same as that in the model reported by Minowa et al. [11]. Under the experimental conditions investigated in this study, tar and char products were formed above a T_{max} of 533 K, but the quantities were quite small. As we cannot analyze the concentrations of tar and char products formed because of their small quantities and their complex chemical structures, we disregarded step 4 in the modeling of cellulose decomposition. According to the stepwise processes of step 1–step 3, we try to derive a mathematical model for the decomposition of cellulose with hot compressed water. It should be noted that we propose a mathematical model which takes the dependence of the rate constants on the temperature variation during the heating and quenching processes into account: we represent the rate constant for each reaction as a function of temperature by using Arrhenius' law.

$$k_i = k_{0i} \cdot \exp\left(-E_{ai}/RT\right) \tag{1}$$

where k_i is the rate constant of the formation and decomposition reaction, and k_{0i} and E_{ai} are the general expressions for the frequency factor and the activation energy of the reaction. R is the gas constant, and T is temperature, which is expressed as a function of time. To calculate the temperature profile, the following equations were used.

$$\text{heating process}: T = v_T \cdot t + T_{init} \tag{2}$$

$$\text{keeping at constant temperature}: T = T_{max} \tag{3}$$

$$\text{quenching process}: \quad T = \frac{6000 \cdot (T_{max} - 273.15)}{t - \left(\frac{T_{max} - T_{init}}{v_T} + t_{Tmax}\right) + 6000} + 273.15 \tag{4}$$

where t is time and T_{init} is the initial temperature, which is set at 303 K as an experimental condition. In Eq. (4), t_{Tmax} means the holding time; the temperature was kept constant at T_{max} for t_{Tmax}. For Eq. (4), there is no actual physical inference, since this equation is used to describe the quenching profile by natural cooling.

According to the assumed decomposition process written as steps 1–3 above, we can assume the following stoichiometric relationships:

$$\text{Cellulose(s)} + 75.7 \cdot \text{H}_2\text{O(l)} \rightarrow 76.7 \cdot \text{Oligomer(l)} \quad ; r_1 \tag{5}$$

$$\text{Oligomer(l)} + 2 \cdot \text{H}_2\text{O(l)} \rightarrow 3 \cdot \text{Monomer(l)} \quad ; r_2 \tag{6}$$

$$\text{Monomer(l)} + \text{H}_2\text{O(l)} \rightarrow \text{Pyrolysis(l)} \quad ; r_3 \tag{7}$$

$$\text{Oligomer(l)} + 2 \cdot \text{H}_2\text{O(l)} \rightarrow 3 \cdot \text{Pyrolysis(l)} \quad ; r_4 \tag{8}$$

In these equations, (s) and (l) mean the state of the materials: (s) is solid state and (l) is liquid state. Cellulose means a crystalline cellulose particle, which consists of an average of 230 molecules of glucose, because the crystalline cellulose used in this study has a viscosity averaged degree of polymerization of 230. It exists in an aqueous phase as a solid state. Oligomer, Monomer and Pyrolysis products mean the general term for oligosaccharides which consist of an average of three units of glucose, monosaccharides which consist of glucose and fructose, and pyrolysis products, respectively. $r_1 \sim r_4$ are the reaction rates of each of the elementary processes. A first-order rate equation can be used for the chemical reactions of each process [25–27].

First we derived a mathematical expression for the cellulose decomposition. As reported by Sasaki et al. [17], a crystalline cellulose particle gradually shrinks at temperatures below 523 K. That is to say, the decomposition reaction of cellulose to oligosaccharides occurs at the particle surface of microcrystalline cellulose. It is a heterogeneous reaction. Therefore, the surface reaction model is used to describe the first process. A representation of the reacting cellulose particle as proposed in this study is shown in Fig. 4. In the mathematical derivation of the kinetic model, it is assumed that a cellulose particle is a spherical shape with an initial particle diameter of r_0. The chemical reaction of cellulose decomposition to oligosaccharides occurs at the surface of the cellulose particle [17, 20]. The decomposition reaction of cellulose is hydrolysis by a water monomer. Water monomers are formed in both the aqueous bulk and the aqueous film near the cellulose particle, but are consumed in hydrolysis reactions at the surface of the cellulose particle. Therefore, a concentration gradient of water monomers is formed near the surface of

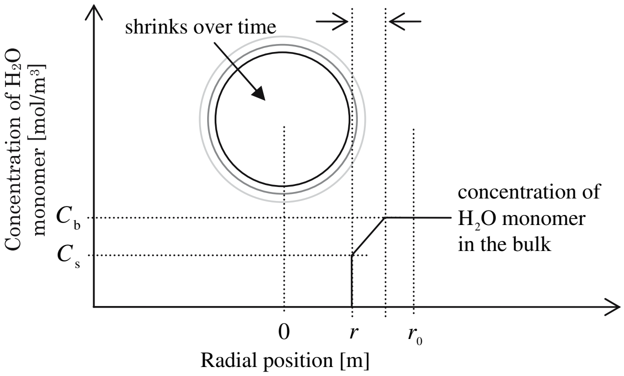

Fig. 4 Representation of the reacting cellulose particle proposed in this study

the cellulose particle. A crystalline cellulose particle has no pores, so a water monomer cannot diffuse into the particle and the concentration of water monomers becomes 0 mol/m^3 at the cellulose particle surface. The following two steps occur in succession during decomposition of a cellulose particle: (A) Diffusion of a water monomer through the aqueous film surrounding a cellulose particle to the surface of the particle, (B) Hydrolysis reaction of a water monomer with a cellulose molecule at the surface of a cellulose particle. For the first mass-transfer step of the water monomer, we assumed a linear driving force approximation for the transportation of a water monomer from the bulk of the water to the surface of a cellulose particle. The mass transfer rate of the water monomer through the aqueous film is as follows:

$$W_A = 4\pi r^2 \cdot k_c(C_b - C_s) \tag{9}$$

where W_A is the mass transfer rate of the water monomer, C_b and C_s are the concentrations of water monomers in the bulk and at the surface of a cellulose particle, respectively, k_c is the mass transfer coefficient of a water monomer through the aqueous film surrounding a cellulose particle, and r is the radial position of the cellulose surface after the reaction has started, which decreases as the hydrolysis reaction progresses. For the second hydrolysis reaction step, we assumed that the hydrolysis reaction rate could be expressed as a first order reaction for water monomers. The hydrolysis reaction rate is expressed as follows:

$$W_B = 4\pi r^2 k_s \cdot C_s \tag{10}$$

where W_B is the hydrolysis reaction rate at the surface of a cellulose particle, and k_s is the first order rate constant, which varies during the reaction according to Eqs. (1)–(4). By assuming a quasi-steady state for the overall process of this cellulose decomposition, it is considered that Eqs. (9) and (10) are equal. In addition, they are considered to be equal to the apparent reaction rate of water monomer for one cellulose particle. Therefore, the following expression can be used:

$$-r_A = 4\pi r^2 \cdot k_c(C_b - C_s) = 4\ \pi\ r^2 k_s \cdot C_s \tag{11}$$

where r_A is the apparent reaction rate of water monomer for one cellulose particle. Eq. (11) can then be rewritten as Eq. (12).

$$-r_A = \frac{4\pi r^2 C_b}{1/\mathrm{k_c} + 1/\mathrm{k_s}} \tag{12}$$

Meanwhile, the decomposition rate is assessed by considering the mass balance of a cellulose particle. At a certain period during the reaction, the radial position of the cellulose surface becomes r, and the molar amount of cellulose particle remaining is $4\pi r^3 \cdot \rho/3$, where ρ is the molar density of the cellulose particle. At that time, the mass balance of the unit cellulose particle is written as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{4}{3}\pi r^3 \cdot \rho\right) = r_B \tag{13}$$

where r_B is the apparent reaction rate of the cellulose molecule for a unit cellulose particle. From the stoichiometric relationship of Eq. (5), r_A $75.7 \cdot r_B$. Therefore, from Eqs. (12) and (13), the following differential equation can be obtained:

$$-4\pi r^2 \cdot \rho \frac{\mathrm{d}r}{\mathrm{d}t} = \frac{4\pi r^2 \cdot C_b}{75.7 \cdot (1/k_c + 1/k_s)} \tag{14}$$

This Eq. (14) is the differential equation which expresses the variation of the radial position of the surface of a cellulose particle over time. We can transform Eq. (14) to a differential equation which expresses the variation in the decomposition ratio of the cellulose particle over time. When the radial position of the surface becomes r, the decomposition ratio of a cellulose particle is written as follows:

$$1 - x = \frac{\frac{4}{3}\pi r^3 \cdot \rho}{\frac{4}{3}\pi r_0^3 \cdot \rho} = \left(\frac{r}{r_0}\right)^3 \tag{15}$$

where x is the decomposition ratio of a unit cellulose particle. By differentiating Eq. (15) with respect to t, we obtain the following relationship:

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{3}{r_0^3} r^2 \frac{\mathrm{d}r}{\mathrm{d}t} \tag{16}$$

By substituting Eqs. (15) and (16) into Eq. (14), we get the following differential equation which expresses the variation in the decomposition ratio of a cellulose particle over time:

$$\frac{4\pi r_0^3}{3} \cdot \rho \cdot \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{4\pi r_0^2 \cdot (1-x)^{2/3} \cdot C_\mathrm{b}}{75.7 \cdot (1/k_\mathrm{c} + 1/k_\mathrm{s})} \tag{17}$$

The decomposition ratio of a cellulose particle can be expressed by the concentration of cellulose molecules according to the following relationship:

$$x = \frac{C_{\mathrm{Cel},0} - C_\mathrm{Cel}}{C_{\mathrm{Cel},0}} \tag{18}$$

where $C_{\mathrm{Cel},0}$ and C_Cel are the concentrations of cellulose molecules at t 0 and t, respectively. By substituting Eq. (18) into Eq. (17) and after simplification, we derive the decomposition rate equation of a cellulose particle as follows:

$$r_\mathrm{Cel} = -r_1 = \frac{\mathrm{d}C_\mathrm{Cel}}{\mathrm{d}t} = -k_1 C_\mathrm{Cel}^{2/3} \tag{19}$$

where r_Cel is the decomposition rate of a cellulose particle and k_1 is the apparent rate constant of cellulose decomposition described as follows:

$$k_1 = \frac{3 \cdot C_{\mathrm{Cel},0}^{1/3} \cdot C_\mathrm{b}}{75.7 \cdot \rho \cdot r_0 \cdot (1/k_\mathrm{c} + 1/k_\mathrm{s})} \tag{20}$$

In the calculation, it should be noted that the calculated concentration of cellulose is set at 0 mol/m^3 after it has obtained a negative value over time.

The mathematical expressions for Oligomer, Monomer, and Pyrolysis products can now be derived. The reaction rates for Eqs. (6)–(8) can be expressed as first order equations for the concentrations of Oligomer and Monomer. Therefore, the variations in the concentrations of Oligomer, Monomer and Pyrolysis products with reaction time can be expressed by the following equations:

$$\begin{aligned} r_\mathrm{Oligo} &= \frac{\mathrm{d}C_\mathrm{Oligo}}{\mathrm{d}t} = 76.7 \cdot r_1 - (r_2 + r_4) \\ &= 76.7 \cdot k_1 C_\mathrm{Cel}^{2/3} - (k_2 + k_4) C_\mathrm{Oligo} \end{aligned} \tag{21}$$

$$r_\mathrm{Mono} = \frac{\mathrm{d}C_\mathrm{Mono}}{\mathrm{d}t} = 3 \cdot r_2 - r_3 = 3k_2 C_\mathrm{Oligo} - k_3 C_\mathrm{Mono} \tag{22}$$

$$r_\mathrm{Pyro} = \frac{\mathrm{d}C_\mathrm{Pyro}}{\mathrm{d}t} = r_3 + 3 \cdot r_4 = k_3 C_\mathrm{Mono} + 3k_4 C_\mathrm{Oligo} \tag{23}$$

where r_Oligo, r_Mono, and r_Pyro are the overall reaction rates of Oligomer, Monomer and Pyrolysis products, respectively. k_2–k_4 are the rate constants for Eqs. (6)–(8), respectively. The rate constants k_2–k_4 also vary during the reaction according to Eqs. (1)–(4).

Variations in the concentrations of each product over time can be calculated by solving the obtained equations. However, it is impossible to solve the obtained equations analytically. Therefore, in this study, we solved the obtained equations numerically. In the numerical calculation, we adopted the fourth-order Runge-Kutta method. The parameters set in the calculation are shown in Table 1. In Table 1, the kinetic parameters such as k_{0i} and E_{ai} were determined in order to fit the calculated lines to the experimental data. The mass transfer coefficient of water monomer, k_c, was calculated from the diffusion coefficient of water monomer, D, and the thickness of aqueous film surrounding a cellulose particle, δ. In the calculation, 1×10^{-8} m^2/s was used as D [30]. The δ can be considered less than 40 μm, because we used the cellulose particle with 80 μm of its average particle diameter and carried out all experiments under vigorous stirring. In the calculation, δ was set on 10 μm. Therefore, k_c was calculated from D/δ as 0.001 m/s. Other parameters shown in Table 1 are the experimental condition.

Figure 5 shows an example of the calculated result. For the calculations shown in Fig. 5, T_max was set at 523 K. The temperature variation for the calculation of Fig. 5, which is calculated from Eqs. (2)–(4) with t_Tmax 0, is shown in Fig. 6. As shown in Fig. 5, the concentration of oligosaccharides shows a plateau above ∼4,000 s. At 4,000 s, the temperature of the system had decreased to about 470 K. This calculated result shows that the oligosaccharides are not decomposed below ∼470 K. This

Table 1 Parameters used in calculating the concentration of each chemical

Parameters	Set value	Unit
E_{a1}	141	kJ/mol
E_{a2}	101	kJ/mol
E_{a3}	129	kJ/mol
E_{a4}	140	kJ/mol
k_{0s}	7.3×10^6	m/s
k_{02}	6.0×10^7	1/s
k_{03}	1.0×10^{10}	1/s
k_{04}	3.0×10^{11}	1/s
k_c	0.001	m/s
T_init	303.15	K
T_max	423.15∼573.15 (/1 K)	K
C_Cel0	0.243	mol/m^3
r_0	8.0×10^{-5}	m
ρ	555	mol/m^3
m_0	0.7	g
MW$_\mathrm{cel}$	41,436.8	–
V	6.93×10^{-5}	m^3
R	8.314	J/(K mol)
h	1	s

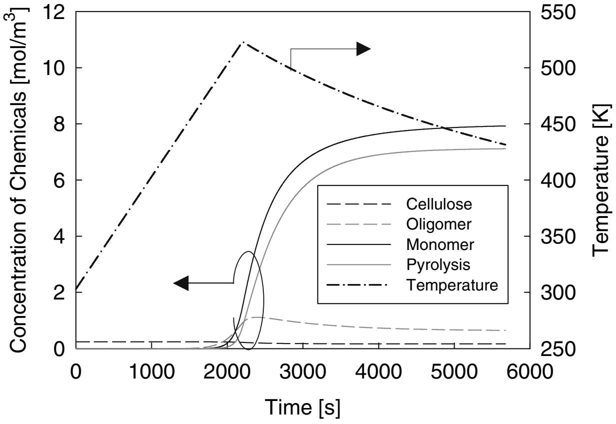

Fig. 5 An example of a calculated result. $T_{\max}$ 523 K, v_T 0.1 K/s, t_{Tmax} 0 s, C_b 7,000 mol/m^3

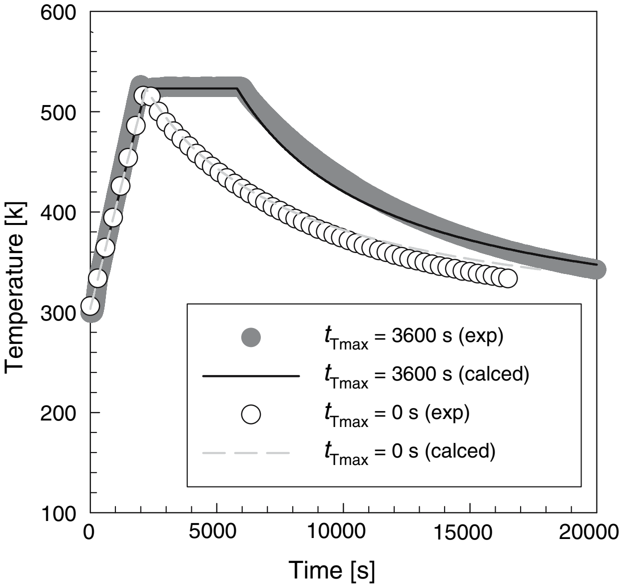

Fig. 6 Temperature profile of the aqueous phase inside the cell. Comparison of experimental and calculated data. The heating rate is 0.1 K/s. The quenching is done by natural cooling

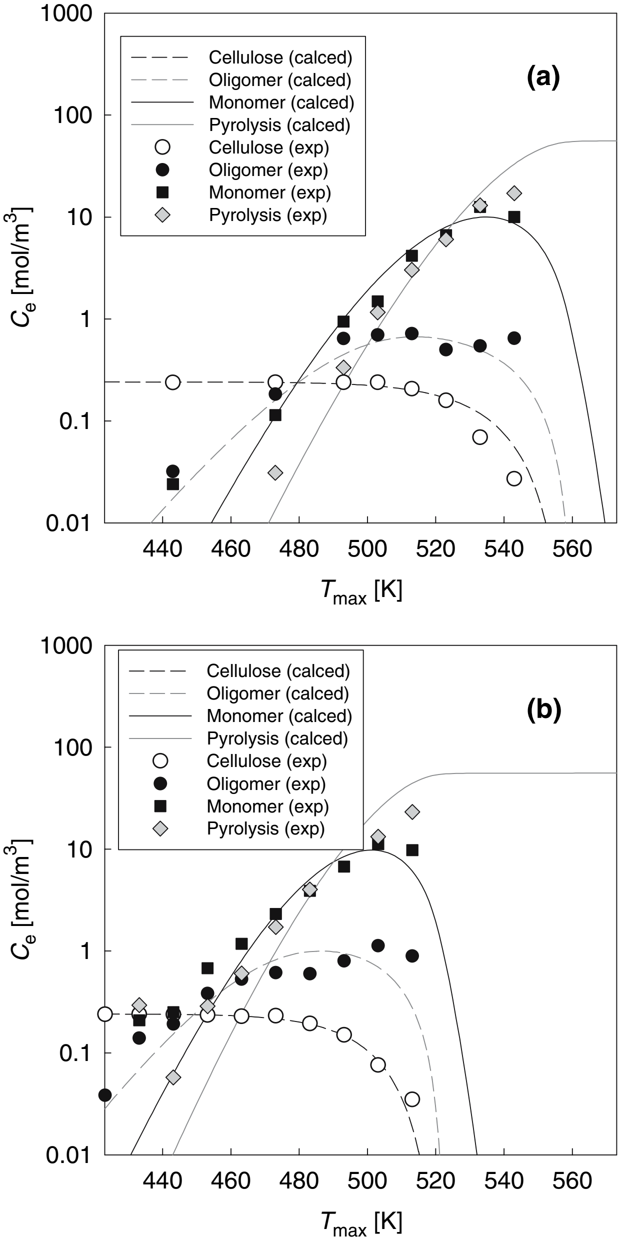

Fig. 7 Effect of $T_{\max}$ on C_e. v_T 0.1 K/s, C_b 7,000 mol/m^3, holding time: t_{Tmax} 0 s (**a**), t_{Tmax} 3,600 s (**b**)

temperature of 470 K is equal to the temperature at which oligosaccharides were detected in Fig. 4. These experimental and calculated results therefore show a reasonable agreement. That is to say, the proposed theoretical model qualitatively illustrates the decomposition reaction of cellulose, and we are going to compare the experimental with the calculated results. Since we could not obtain the reactant concentrations from our batch system in the middle of the operation, we investigated the effect of $T_{\max}$ on the concentration of chemicals after the reaction had stopped. In the calculation, we defined the concentration of chemicals when T had decreased to 303 K as the concentration of chemicals after the reaction, C_e. For various $T_{\max}$, the concentration profiles, which are like those shown in Fig. 5, were calculated, and C_e values were determined for each $T_{\max}$. They are plotted in Fig. 7 together with the experimental results. Fig. 7a shows the relationship between the C_e of chemicals and $T_{\max}$ under t_{Tmax} 0 s. As shown in Fig. 7a, a reasonable agreement of theoretical to experimental data is obtained.

Subsequently, we investigated the effect of t_{Tmax} for the decomposition of cellulose with hot compressed water. The experimentally obtained and calculated temperature profiles for t_{Tmax} 3,600 s are shown in Fig. 6. The calculated temperature profile well follows the experimental data. Fig. 7b shows the relationship between C_e and $T_{\max}$ when

Table 2 Activation energies and frequency factors as obtained from a literature study

Reaction	Puressure (MPa)	E_a (kJ/mol) frequency factor	Literature
Cellulose decomposition	30	136* 7.28×10^{6}*	Sasaki [31]
Cellobiose hydrolysis	25	91** 2.83×10^{7}**	Sasaki et al. [25]
Glucose decomposition	25–30	96 2.57×10^{11}***	Kabyemela et al. [26]
	25	88 –	Amin et al. [32]
	25	121 –	Bobleter and Pape [33]
	25	121 1.33×10^{10}	Matsumura et al. [34]
Cellobiose pyrolysis	25	122.6 1.26×10^{10}	Sasaki et al. [25]

* calculated from given data in Sasaki [31]

** calculated from given data in Sasaki et al. [25]

*** calculated from given data in Kabyemela et al. [26]

t_{Tmax} is 3,600 s. The calculated result also follows the experimental data well. From the result, it is suggested that the proposed model would be useful to predict the relationship between C_e and $T_{\max}$ obtained from the operation with a constant flow stirred tank reactor (CSTR); the t_{Tmax} is regarded as a retention time for CSTR. In addition, comparing Fig. 7a and b, we can see that large amount of cellulose was decomposed at lower temperature when the temperature was hold at $T_{\max}$ for 1 h. This result indicates that we can estimate the suitable condition for liquefaction of cellulose.

Finally, we will evaluate the validity of the activation energy and the frequency factor, which are listed in Table 1. In Table 2, the activation energy and frequency factor, which were reported in or determined from the previously reported papers, is shown. As shown in Table 2, the E_{ai} and k_{0i} values show a good agreement with those used in this study. This result demonstrates the validity of the E_{ai} and k_{0i} values used in this study.

Conclusion

In this study, we investigated the cellulose liquefaction in hot compressed water by using a batch reactor, which is preferable to liquefy a large amount of solid sample, but requires slow heating and quenching processes. A micro-crystalline cellulose decomposes to oligosaccharides with a high degree of polymerization, and the produced oligosaccharides decompose down up to monosaccharides and pyrolysis products. According to the predicted decomposition mechanism, the mathematical model which involves the effect of temperature variation during the reaction was derived. The calculated results showed a reasonable agreement to the experimental data. The used parameters for the calculation also gave a good correlation to those reported in the literatures. In conclusion, it was indicated that the proposed decomposition mechanism of cellulose and the derived mathematical model were appropriate. The mathematical model should be applicable to a practical process of liquefaction of wood biomass.

Acknowledgement This study was supported in part by a Grant-Aid from The Ministry of Education, Culture, Sports, Science and Technology of Japan.

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