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Measurement of the hydrothermal reaction rate of cellulose using novel liquid-phase thermogravimetry

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Abstract

This paper deals with the use of liquid-phase thermogravimetry to investigate the reaction kinetics of cellulose in hot compressed liquid water. The liquid-phase thermogravimetric measuring system employed in this study is equipped with a magnetic suspension balance that can measure the weighing force without contact. Thus, a high pressure and temperature reactor is used, with the main body of the balance located outside the reactor. Using this system, the cellulose weight decay was observed under isothermal and nonisothermal conditions over a temperature range up to 300°C at 10 MPa. The weight decay rate obtained obeyed first-order kinetics, with its activation energy around 220 kJ/mol. The kinetic constants obtained in this study were found to be reasonable when compared to previously reported parameters.

Keywords: Cellulose; Hydrothermal reaction; Magnetic suspension balance; Reaction kinetics; Thermogravimetry

1. Introduction

Processes for the conversion of cellulosic biomass into recycled resources, e.g., chemicals and energy, are attracting great attentions [1–5]. The use of hot compressed liquid water is expected to be one of the processing methods for the conversion of cellulosic biomass into sugars from which useful chemical products can be produced through chemical and fermentative processes [6]. Water itself works as an acid at higher temperature ranges. It efficiently reacts with carbohydrates, through hydrolysis, without any other catalyst. The reaction in hot compressed water, the so-called hydrothermal reaction, has not yet been investigated in detail. Further, an understanding of the mechanisms and kinetics under hydrothermal conditions is needed for proper design of the conversion processes. However, conventional experimental methods, in which batch or semi-batch systems are usually employed, involve complicated procedures.

Thermogravimetry (TG) was developed for the real-time measurement of weight changes that occur with temperature. It provides useful information for chemical reactions, physical phenomena, and so on. However, common TG systems are designed to make measurements in the gas phase including under vacuum conditions, and difficulties arise when these systems are used for measurements in the liquid phase, especially under high temperature and pressure

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conditions. The main challenge to making measurements in the liquid phase is the direct contact between the measuring cell and the weighing device as the weighing device is susceptible to damage, by the measuring atmosphere. Magnetic suspension balances, however, have advantages over conventional direct-contact weighing devices in this respect, as they allow for contactless measurement [7]. These balance have, therefore, been employed in several gravimetric systems for measurement under extreme conditions. To observe the hydrothermal reaction kinetics, the magnetic suspension balance is applied to a liquid phase thermogravimetric system as a weighing device.

The objectives of the present study were to establish a real-time weighing method and to observe the reaction kinetics of cellulose, a major component of vegetable biomass, under hydrothermal conditions. The measurement of weight changes of a submerged sample is discussed, including the issue of buoyancy corrections. The decomposition of cellulose in hot compressed liquid water illustrates an application of the proposed system.

2. Apparatus

The basic principle of the magnetic suspension balance was discovered in the middle of the 1940s [8]. Through a development of the method to control its magnetic field [9], a practical system was proposed by Wagner and his co-worker in 1991 [10]. At present, magnetic suspension is employed in commercially available units [7]. Such gravimetric instruments have been used successfully for high-pressure gas adsorption [11], corrosive gas adsorption [12], high precision density measurements [13], weighing in ultrahigh vacuum [14] and high-pressure TG [15]. The authors employed the magnetic suspension balance as the weighing device in a liquid-phase thermogravimetric system.

Fig. 1 provides a schematic diagram of the liquid phase thermogravimetric measuring system (Rubotherm and BEL Japan) employed in this study. The magnetic suspension balance consists of a supporting electromagnet, a suspension permanent magnet, a position sensor, a set point controller, a measurement load cage and an electric balance. The

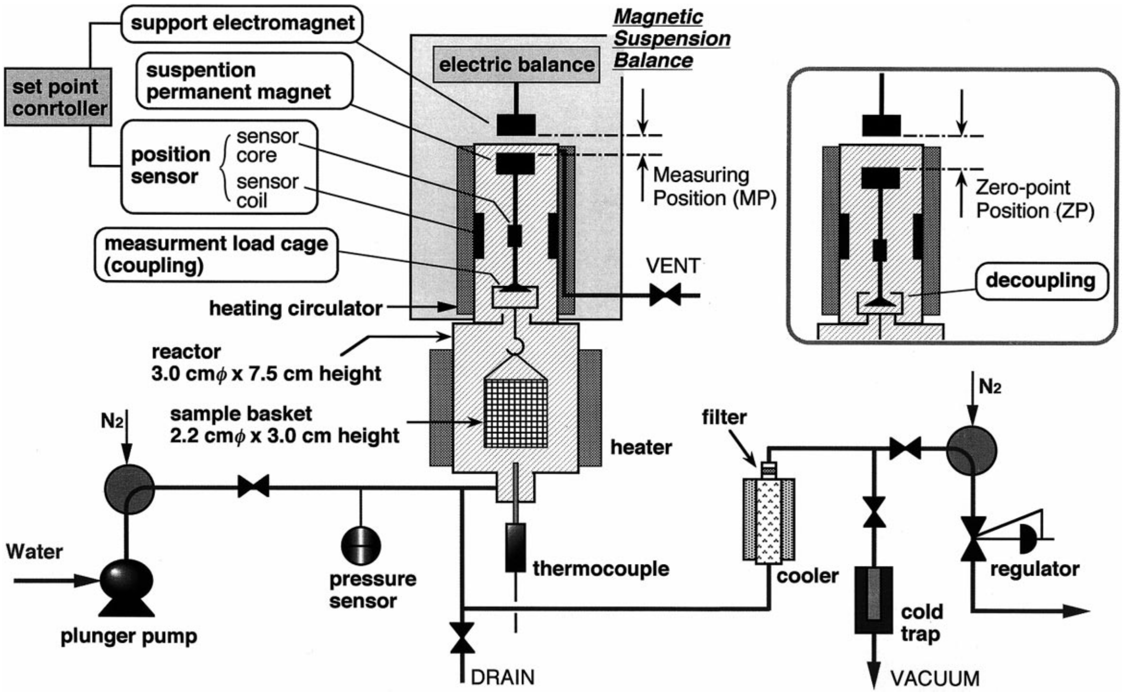

Fig. 1. A schematic diagram of the liquid phase thermogravimetric system using a magnetic suspension balance.

electromagnet, which is attached to the electric balance, maintains the suspended state of the permanent magnet. This magnetic suspension coupling transmits the measuring force to the balance located outside the chamber without direct contact. Use of the magnetic suspension balance, therefore, makes weighing possible under extreme conditions, e.g., hydrothermal conditions. In addition, the measuring load can be decoupled from the balance whenever required, lowering the position of the permanent magnet a few millimeters below the measuring position (MP). This position (zero-point position: ZP) corresponds to an empty balance pan in a normal weighing procedure and allows the user to tare and calibrate the balance. The coupling housing was made of an alloy of $CuBe_2$, and the reactor, pipelines, and sample holder (basket) were made of stainless steel (SUS 316). The system was designed to withstand temperatures up to 300°C and pressures up to 10 MPa. However, the operation temperature range of the coupling housing was limited to below 250°C to avoid the influence of temperature on the magnetic force. Therefore, all measurements at a temperature of 250–300°C were carried out keeping the coupling housing at 250°C, while the housing and reactor were controlled to the same temperature when operating at a temperature lower than 250°C. An electric balance (Mettler: AT 261) was used as a force-measuring device. The balance operation, heating control, and data collection (indicated weight, temperature, and pressure) could be automated by a personal computer.

3. Experimental procedure

The test specimen was put into the sample holder, and the holder was hung on a hook connected on the measuring load cage. When measuring a powdered sample, a fiberglass thimble filter (ADVANTEC: 88R) was inserted into the holder to prevent the powder from dropping. The initial sample weight is measured under vacuum. Deionized water is compressed up to the pressure required (10 MPa) at room temperature and then fed into the system with a plunger pump. A backpressure regulator controls the pressure. Changes in indicated weight are recorded as the temperature is elevated. In this study, both isothermal and dynamic experiments were performed.

Two types of commercial cellulose were used, namely, microcrystalline (MERCK) and filter paper (ADVANTEC). For the test of the cellulose microcrystalline, a fiberglass thimble filter was inserted into the sample holder. The filter paper was chopped up into 5 mm squares. Both samples were dried at 378 K prior to the experiment. Inert crushed quartz glass was also tested to examine the buoyancy correction.

4. Results and discussion

4.1. Buoyancy correction

It is necessary to correct the sample weight for buoyancy. Thus, the buoyancy correction was carried out as follows.

Changes in the indicated weight with temperature, pressure, and time can be obtained. From the temperature, T, and pressure, p, the water density can be determined from the steam table [16]. The buoyancy effect on the sample holder is $m_h g\rho_w/\rho_h$. The weighing force of the holder under the submerged condition, F_h, can be expressed as:

$$F_h = m_h g - \frac{m_h g \rho_w}{\rho_h} \tag{1}$$

where g, m_h, ρ_h, and ρ_w are gravitational acceleration, holder mass, holder density, and water density, respectively. Subtracting this force from the indicated weight, I, gives the weighing force of the sample in water, F_s, as the following expression:

$$F_s = I - F_h \tag{2}$$

Both $m_s g\rho_w/\rho_s$ and $m_s g - F_s$ represent the same value which expresses the sample buoyancy, where m_s and ρ_s are sample mass and sample density, so that Eq. (3) can be obtained. Transforming this equation, Eq. (4) is given to express the sample mass.

$$\frac{m_s g \rho_w}{\rho_s} = m_s g - F_s \tag{3}$$

$$m_s g = \frac{F_s}{1 - \rho_w/\rho_s} \tag{4}$$

Fig. 2 shows the results of this buoyancy correction for a measurement of inert quartz glass. Keeping the pressure at 10 MPa, the reactor was heated up to 250°C. The indicated weight, i.e., the apparent total

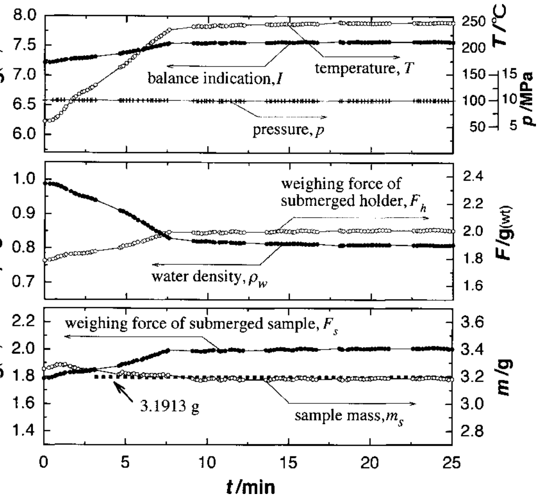

Fig. 2. Buoyancy correction for the measurement of quartz glass.

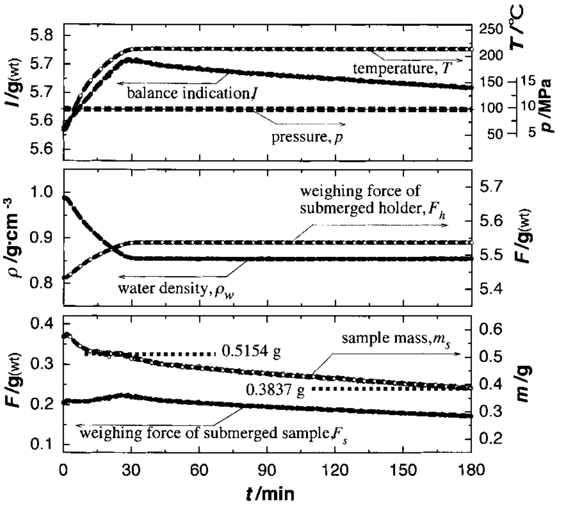

Fig. 3. Buoyancy correction for the measurement of cellulose.

weighing force increased with the increase in the temperature because the decrease in water density weakened the buoyancy. The change in water density could be estimated from the collected temperature and pressure data. Then the weighing force of the submerged holder was obtained using the water density; the weighing force of the submerged sample could be then obtained by subtracting that of the submerged holder from the total weighing force. The corrected sample mass was calculated from the sample weight in water using Eq. (4) with the densities of water and quartz glass. The values for the sample mass were constants corresponding with the initial sample weight measured in vacuum, 3.1913 g. The disagreement in the early stage is caused likely by the effects of convection, that is, the convection with increase in temperature produced a flux that pushed the sample and/or holder down and increased the apparent weight. This kind of problem with conventional TG measurements has been discussed for several decades, as has the effects of buoyancy [17], and TG instruments have been developed to reduce/prevent such effects. For this liquid-phase measurement, unfortunately, much remains to be investigated in order to solve this problem with better design and operation. So far, the experimental data have been dealt with in this paper, taking into consideration the convection effect involved in the shapes of the curves. Incidentally, this type of buoyancy correction is legitimate under the limitation that changes in the density of the holder and sample can be neglected. It was confirmed in the present study that the density of quartz glass does not change significantly, nor does that of the sample holder as well. On the other hand, the cellulose density does change; for example, the carbonization of cellulose increases the sample density. In fact, an increase in the density of a residue was observed as the reaction proceeded. However, the change was relatively small, especially at lower temperatures. The result of this buoyancy correction for cellulose decomposition is illustrated in Fig. 3. As can be seen, the beginning and end of the corrected curve agree with the masses of the initial sample and residue, respectively. The density of the residue was almost the same as that of cellulose, i.e., approximately 1.5 g/cm^3, therefore, the change in the sample density was slight enough to be neglected. It was also estimated that the effect on the buoyancy of the increase in soluble matter along with the cellulose decomposition was not more than 0.5% in the weighing force error.

4.2. Cellulose decomposition

Some of the results obtained from the isothermal decomposition tests for cellulose (filter paper) at 10 MPa are illustrated in Fig. 4, where the moment that the temperature reaches the set point is applied as the starting time, i.e., t=0. The semi-logarithmic plot

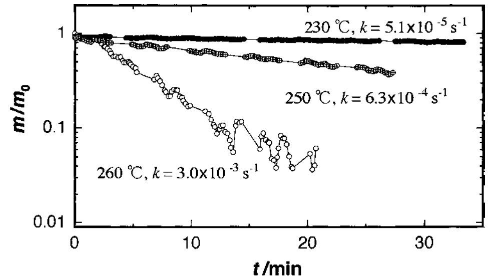

Fig. 4. Weight decay curves for cellulose decomposition at 10 MPa.

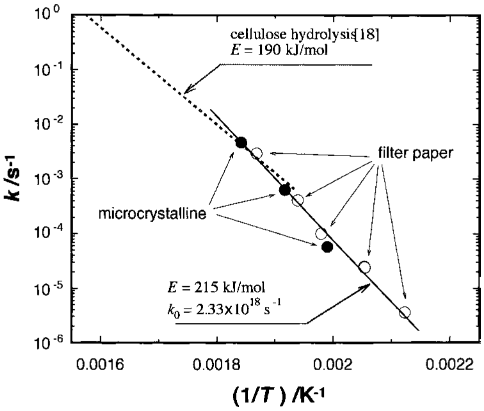

Fig. 5. The Arrhenius plot for the weight decay of cellulose in hot compressed liquid water at 10 MPa.

of reduced weight against time exhibits a straight line for every result. The weight decay of cellulose was found to be a first-order reaction, and the rate constant could be determined from the slope of the line. Fig. 5 shows the Arrhenius plot for the cellulose decomposition rate in hot compressed water, and the activation energy was determined to be 215 kJ/mol. The previously reported rate for cellulose hydrolysis, which was obtained under a semi-batch system [18], is also shown in the same figure. The activation energy for this cellulose hydrolysis was approximately 190 kJ/mol. As can be seen, the data for these two reactions almost coincide; therefore, the kinetic constants obtained in this measurement can be concluded to be reasonable for expressing the cellulose hydrolysis rate. As the kinetic constants for both the microcrystalline and filter paper exhibited a single line, the effect of the shape/size of cellulose on its decomposition rate appeared to be quite small for this measurement. In addition, the carbon balances for each reaction of the filter paper are summarized in Table 1. The amount of total organic carbon (TOC) dissolved in the liquor collected after the measurement was found to almost correspond with the amount of carbon that had come off the cellulose sample in the lower temperature experiments. When tests were performed at higher temperatures, i.e., more than 250°C, the material balance showed a disagreement, the reason for which is that the production of oily substances, which are difficult to collect, increases with increase in the operating temperature.

Fig. 6 shows the reduced weight, m/m_0, versus temperature for dynamic experiments, the so-called TG curves, at different heating rates carried out using the filter paper. Various methods have been developed for the kinetic analysis of TG curves. One of them was applied to analyze the TG curves obtained in this study. This method, which was proposed by Suzuki and his co-workers [19], utilized the half-decomposed temperature, $T_{1/2}$, to determine the kinetic parameters. The half decomposed temperature refers to the tem-

Table 1
Carbon balance for cellulose decomposition (filter paper)[a]

T (°C)	k (s^{-1})	m_{C0} (g)	m_C (g)	$m_{C0}-m_C$ (g)	m_{DOC} (g)	$m_{DOC}/(m_{C0}-m_C)$
198	3.58×10^{-6}	0.440	0.427	0.013	0.015	1.15
214	2.42×10^{-5}	0.229	0.170	0.059	0.062	1.05
214	2.52×10^{-5}	0.636	0.485	0.151	0.143	0.947
232	1.01×10^{-4}	0.452	0.289	0.163	0.166	1.02
243	4.10×10^{-4}	0.514	0.034	0.480	0.394	0.821
262	2.95×10^{-3}	0.830	0.028	0.802	0.405	0.505
300[b]	–	0.422	0.005	0.437	0.260	0.595

[a] m_{C0}: mass of carbon in the initial sample, m_C: mass of carbon in the residue, m_{DOC}: mass of dissolved organic carbon in the liquor.
[b] Result of dynamic experiment at θ=3°C/min.

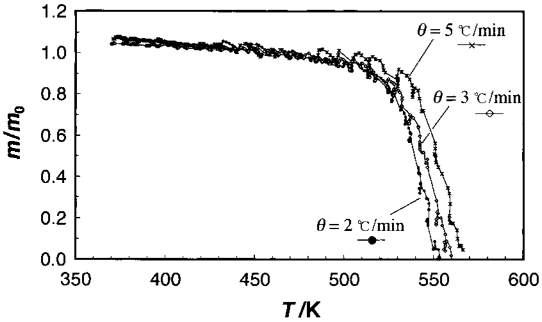

Fig. 6. TG curves for cellulose decomposition in hot compressed liquid water at 10 MPa.

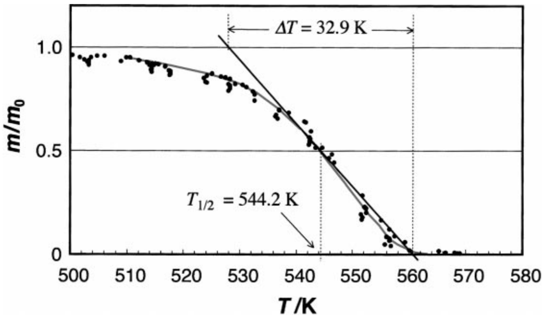

Fig. 7. Definition of $T_{1/2}$ and ΔT from a TG curve for cellulose decomposition.

perature at the time when half amount of the sample has decomposed. The rate of a first-order reaction can generally be expressed as:

$$\frac{dx}{dt} = k(1 - x) \tag{5}$$

where x is the conversion fraction. This rate equation is transformed into Eq. (6) using $dx/(1{-}x) = -dm/m$, the Arrhenius equation, $k = k_0 \exp(-E/RT)$, and the heating rate, $\theta = dT/dt$.

$$\frac{dm}{m} = -\frac{dx}{1 - x} = \left(-\frac{k_0}{\theta}\right)\exp\left(-\frac{E}{RT}\right) dT \tag{6}$$

Integration of the above equation gives:

$$\frac{m}{m_0} = \exp\left\{\frac{k_0 E}{\theta R} E_1\left(\frac{E}{RT}\right) - \frac{RT}{E}\exp\left(\frac{-E}{RT}\right)\right\} \tag{7}$$

where

$$E_1(z) = \int_z \left[\frac{\exp(-z)}{z}\right] dx \tag{8}$$

and $z = E/RT_{1/2}$. When comparing Eq. (7) with an experimentally obtained TG curve, the value of $T_{1/2}$, and the tangent at $T = T_{1/2}$, which defines ΔT, are used to interpret the TG data. Using $\psi(z) = 1 - z\exp(z)E_1(z)$, $\xi \equiv \Delta T/T_{1/2}$ is derived from Eq. (7) as the following equation:

$$\xi \equiv \frac{\Delta T}{T_{1/2}} = \left(\frac{2}{\ln 2}\right)\psi\left(\frac{E}{RT_{1/2}}\right) \tag{9}$$

The value of ξ is obtained from experimentally determined $T_{1/2}$ and ΔT, as exemplified in Fig. 7 for the operation $\theta = 3$°C/min, and $\psi(z)$ is then calculated from Eq. (9). The activation energy, E, is evaluated using the value of z, which can be determined by a previously prepared diagram to show the relationship between $\psi(z)$ and z [19]. The pre-exponential factor, k_0, is readily obtained from Eq. (10).

$$k_0 = \left(\frac{2\theta}{\Delta T}\right)\exp\left(\frac{E}{RT_{1/2}}\right) \tag{10}$$

It is undeniable that there exists a certain error in the definition of the tangent that gives ΔT, because the TG curves are not smooth in shape. Therefore, we examined the effects of the error in ΔT on the kinetic parameters obtained though this process.

For example, Fig. 8 illustrates the results of our analysis of the TG curve for $\theta = 3$°C/min, setting positive and negative 10% errors in the value of ΔT. The value of E decreased almost in proportion to the

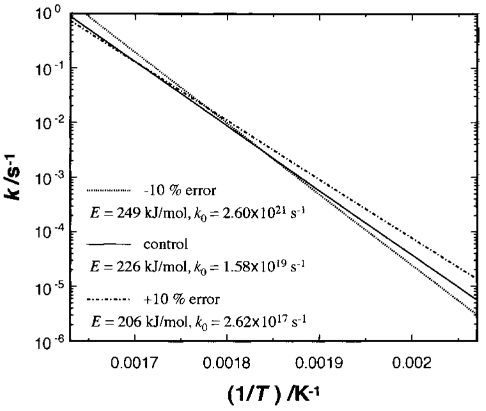

Fig. 8. Effects of the error in ΔT on the determination of kinetic parameters.

Table 2
Summary of activation energies and pre-exponential factors obtained

θ (K/min)	$T_{1/2}$ (K)	ΔT (K)	E (kJ/mol)	k_0 (s^{-1})
2.0	539.4	30.0	233	8.51×10^{19}
3.0	544.2	32.9	226	1.58×10^{19}
5.0	551.5	34.3	225	9.27×10^{18}
Isothermal	–	–	215	2.33×10^{18}

increase in ΔT, and the value of k_0 also changed. The changes in values of E and k_0 offset each other. The error in ΔT did not appear to have any serious effects on the determination of the rate constant, k, over the significant temperature range, i.e., around 200–300°C.

The values of E and k_0 obtained from this process are given in Table 2 with those from the Arrhenius plot for isothermal tests. With increases in the heating rate, the value of $T_{1/2}$ tended to increase and the value of ΔT widened; however, the differences in the obtained values of E and k_0 were small. Fig. 9 shows a comparison of the dependency of the rate constant on temperature between the result of the series of isothermal tests and those calculated from the values of E and k_0 estimated in the dynamic analysis. The values almost coincide, though the calculated lines from the dynamic analysis appear to be slightly lower than the interpolated line of the isothermal tests in the coordinate. It was found that the TG curves obtained in this study give reasonable kinetic parameters for the hydrolysis of cellulose. It can be concluded that the use of the proposed liquid-phase thermogravimetric measuring system simplifies the process of determining the kinetic parameters of hydrothermal reactions.

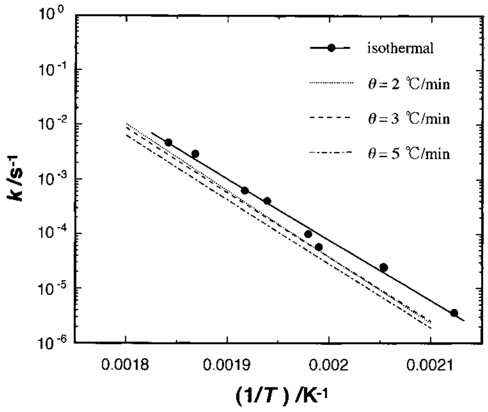

Fig. 9. Comparison of k vs. $1/T$ between the results of isothermal and dynamic experiments.

5. Conclusion

Kinetic parameters for the hydrothermal reaction of cellulose were successfully obtained by the proposed liquid phase thermogravimetric system. Compared with previously reported parameters, the obtained values of the activation energy and pre-exponential factor were found to be reasonable in describing cellulose hydrolysis, though they were basically evaluated based on the overall weight decay rate of cellulose. Furthermore, it was suggested that the use of this system simplifies the process of determining hydrothermal kinetic parameters. This measuring method is expected to reduce the complications in the experimental work related to hydrothermal reactions. Investigations of the conversion of real cellulosic biomass, including waste wood, old paper, and agricultural waste products, in hot compressed water are promising applications of this method. Every real cellulosic biomass has as major components not only cellulose but also hemicelluloses and lignins, so that its reaction mechanism is more complicated than that of pure cellulose. Even for such a multi-composed material, however the use of the liquid phase thermogravimetric system should enable the behavior of the hydrothermal reaction to be observed simply.

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References

[1] D.A. Nelson, P.M. Molton, J.A. Russell, R.T. Hallen, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 471.
[2] K.V. Kruse, For. Prod. J. 45 (9) (1995) 82.
[3] J.U. Delgado, G.A. Giraldo, Biomass Bioenergy 8 (1995) 21.
[4] S.J.B. Duff, W.D. Murray, Bioresource Tech. 55 (1996) 1.
[5] C. Yokoyama, Nihon Enerugi Gakkaishi 76 (1997) 853.

[6] K. Arai, Enerugi Shigen 16 (1995) 175.
[7] K. Nakai, Adsorption News 112 (1997) 10.
[8] J.W. Clark, Rev. Sci. Instr. 18 (1947) 915.
[9] Th. Gast, Naturwissenschaften 56 (1969) 434.
[10] H.W. Losch, R. Kleinrahm, W. Wagner, in: J. Stanbury (Ed.), Verfabrenstechnik und Chemieingenieurwesen, GVC Düsseldorf, 1994, p. 117.
[11] W. Duschek, R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. 22 (1990) 827.
[12] F. Dreisbach, R. Staudt, M. Tomalla, J.U. Keller, in: M.D. LeVan (Ed.), Fundamentals of Adsorption, Kluwer Academic Publishers, Dordrecht, 1995, p. 259.
[13] W. Wagner, K. Brachthauser, R. Kleinrahm, H.W. Losch, Int. J. Thermophys. 16 (1995) 399.
[14] Th. Gast, E. Robens, J. Thermal Analysis 47 (1996) 605.
[15] Th. Gast, W. Pahlke, J. Thermal Analysis 37 (1991) 1933.
[16] L. Haar, J.S. Gallagher, G.S. Kell, NBS/NRC Steam Tables, Hemisphere, Washington, DC, 1984.
[17] J.P. Czarnecki, N. Koga, V. Šesták'ova, J. Šesták, J. Thermal Analysis 38 (1992) 575.
[18] T. Adschiri, S. Hirose, R. Malaluan, K. Arai, J. Chem. Eng. Jpn. 26 (1993) 676.
[19] M. Suzuki, D.M. Misic, O. Koyama, K. Kawazoe, Chem. Eng. Sci. 33 (1978) 271.