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Estimation of kinetic triplet of cellulose pyrolysis reaction from isothermal kinetic results

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Abstract−This paper presents a new approach to estimate the Arrhenius parameters as well as the reaction model function of cellulose pyrolysis reaction. Reduced time plot (RTP) was employed to choose a proper form of reaction model function for cellulose pyrolysis reaction. A state-of-the-art thermobalance (TB) that is able to form real isothermal reaction conditions was introduced to construct RTPs from isothermal decomposition kinetic data. The reaction model function of cellulose pyrolysis reaction would be accounted for by Avrami-Erofeev function, $n(1-\alpha)\{-\ln(1-a)\}^{1-1/n}$ where n is determined to be 3.69.

Key words: Pyrolysis, Isothermal Kinetics, Cellulose, Reaction Model Function, Avrami-Erofeev Function

INTRODUCTION

Shortages of fossil fuel as well as growing environmental concerns have rekindled interest in using renewable energy sources more extensively. Biomass is one of the most promising renewable energy sources because of its versatile application potentials. In this regard, pyrolysis has drawn much attention owing to its ability to acquire fuel and valuable chemicals from biomass. Since dry biomass fuels typically are comprised of about 50% cellulose by weight, the study of the pyrolysis kinetics of cellulose is essential to the process design of biomass pyrolysis.

A great many investigators have dealt with cellulose pyrolysis kinetics. The power law equation with a reaction order of one has been adopted as the reaction model function of cellulose pyrolysis without confirmation [Agrawal, 1988a, b; Antal and Varhegyi, 1995; Bigger et al., 1998; Blasi, 1994; Bradbury et al., 1979; Broido, 1976; Conesa et al., 1995; Diebold, 1994; Gronli et al., 1999; Varhegyi and Antal, 1989; Varhegyi et al., 1994, 1997]. In the companion paper [Eom et al., 2005], we checked whether or not the first-order reaction would be proper to represent the cellulose pyrolysis kinetics. Applying the constraint of the first-order kinetics [Eom et al., 2005] gave rise to the similar Arrhenius parameters to similar those reported by the previous studies [Agrawal, 1988b; Antal and Varhegyi, 1995; Gronli et al., 1999; Varhegyi and Antal, 1989; Varhegyi et al., 1994, 1997]. However, the reaction order was estimated to be about 1.5 without constraint on the reaction order. Also, the disparities of the Arrhenius parameters were apparent. Owing to correlation among the kinetic parameters, fixation of reaction order forces the Arrhenius parameters to deviate from the real ones.

We also noticed that differences in activation energy values between model-fitting and model-free methods could imply the inappropriateness of the power law equation to describe the reaction model of cellulose pyrolysis. It is essential to derive a correct form of reaction model function for cellulose pyrolysis reaction.

RTP requiring isothermal kinetic data is expected to be one of the reliable tools to determine the reaction model of thermal decomposition of solids [Bamford and Tipper 1980; Halikia et al., 1998; Rodante et al., 2002; Vyazovkin and Wight, 1999]. However, most isothermal kinetic studies have suffered from uncertainty arising from decomposition within non-isothermal regions that would be formed during the course of reaching a target temperature, possibly leading to deviation from real isothermal conditions [Maciejewski, 2000]. In order to avoid undergoing non-isothermal decomposition regions, we introduced a state-of-the-art thermobalance (TB) which is able to monitor isothermal pyrolysis kinetics without undergoing temperature rise of reaction zone to achieve a target temperature [Kwon et al., 1988].

This paper derives a reaction model of cellulose pyrolysis reaction using RTPs acquired from isothermal kinetic experiments under true state conditions and, consequently, to estimate the Arrhenius parameters.

THEORETICAL

Based on single step kinetics, the kinetic equation for solid state decomposition is denoted by:

$$\frac{d\alpha}{dt}=k(T)f(\alpha) \tag{1}$$

Arrhenius equation generally expresses the explicit temperature dependency of the rate constant:

$$\frac{d\alpha}{dt}=A\exp(-E/RT)f(\alpha) \tag{2}$$

The A, E, and f(α) are called as kinetic triplet that can characterize a unique pyrolysis reaction.

The reaction model may take various forms, some of which are shown in Table 1.

RTP was introduced to determine the reaction model. The RTP was developed by plotting α as a function of a reduced time, t/t_α, where t_α is the time that it takes to attain a specific conversion (α= 0.9). In order to choose appropriate reaction model for cellulose pyrolysis reaction, we compared experimental RTPs with theoreti-

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Table 1. Reaction models employed to describe the solid state reaction

	Reaction model	f(x)	g(x)
1	Power law	$4x^{3/4}$	$x^{1/4}$
2	Power law	$3x^{2/3}$	$x^{1/3}$
3	Power law	$2x^{1/2}$	$x^{1/2}$
4	Power law	$2/3x^{-1/2}$	$x^{3/2}$
5	One-dimensional diffusion	$1/2x^{-1}$	x^{2}
6	Mample (first-order)	$1-x$	$-\ln(1-x)$
7	Avrami-Erofeev	$4(1-x)[-\ln(1-x)]^{3/4}$	$[-\ln(1-x)]^{1/4}$
8	Avrami-Erofeev	$3(1-x)[-\ln(1-x)]^{2/3}$	$[-\ln(1-x)]^{1/3}$
9	Avrami-Erofeev	$2(1-x)[-\ln(1-x)]^{1/2}$	$[-\ln(1-x)]^{1/2}$
10	Three-dimensional diffusion	$2(1-x)^{2/3}(1-(1-x)]^{1/3})^{-1}$	$[-\ln(1-x)^{1/3}]^{2}$
11	Contracting sphere	$3(1-x)^{2/3}$	$1-(1-x)^{1/3}$
12	Contracting cylinder	$2(1-x)^{1/2}$	$1-(1-x)^{1/2}$
13	Second-order	$(1-x)^{2}$	$(1-x)^{-2}-1$

cal ones.

After identifying the reaction model, one can determine the rate constant at a temperature from the slope of a plot of $g(\alpha)$ versus t, which can be obtained from integrating Eq. (1) as follows:

$$g(\alpha)=k(T)t \tag{3}$$

The rate constants are assayed at various temperatures and the Arrhenius plot is used to determine Arrhenius parameters:

$$\ln k(T_i)=\ln A-\left(\frac{E}{R}\right)\frac{1}{T_i} \tag{4}$$

EXPERIMENTAL

Purely refined cellulose powder with an average diameter of 20-100 μm was used in this study and supplied by Daejung Chemical & Metals Co., Ltd. (BG24EC Powder). The samples were dried in a desiccator at 120 for 24 hours before analyses.

For dynamic operations, thermogravimetric analyzer (Model: SDT-2960 manufactured by TA Instruments Co.) was used and the loading amount of sample was 7±0.1 mg. Temperature was raised up to 923 K with three linear heating rates of 5, 10, and 20 K min^{-1}. Nitrogen was used as a carrier gas at a flow rate of 50 mL min^{-1}.

TB was used for isothermal kinetic experiments (Fig. 1). The TB consisted of a laboratory scale pyrolysis reactor and a weight detection unit. A high stainless steel tube (5.5 cm i.d.×1.0 m) was used as a pyrolysis reactor. The reactor was heated to a reaction temperature under a stream of nitrogen with a linear velocity of 8.3 cm/sec, yielding a laminar flow (Re<100 at most reaction temperatures). Cellulose samples were suspended in a 100 mesh stainless steel wire basket. The sample basket was connected to an electric balance (Satorius BP61) by a 0.3 mm diameter nichrome wire. The balance was lowered down quickly by a winch to insert sample to a reaction zone after a reaction temperature was stabilized. Hence, there is no delay to reach a target temperature. Under immediate static conditions, weight loss of a sample with respect to time was recorded continuously over time by an on-line personal computer. Since the heat transfer may impede chemical kinetics at the initial stage of reaction, we reduce the size of sample as small as possible. About 10 mg of cellulose sample was applied to the TB at the isothermal operating temperatures of 633, 638, and 643 K.

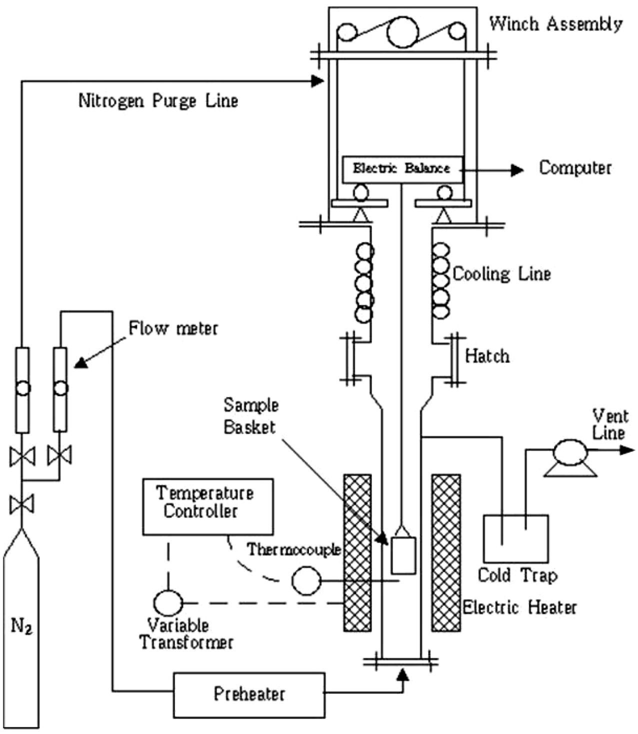


Fig. 1. Schematic diagram of thermobalance operated under isothermal conditions.

RESULTS AND DISCUSSION

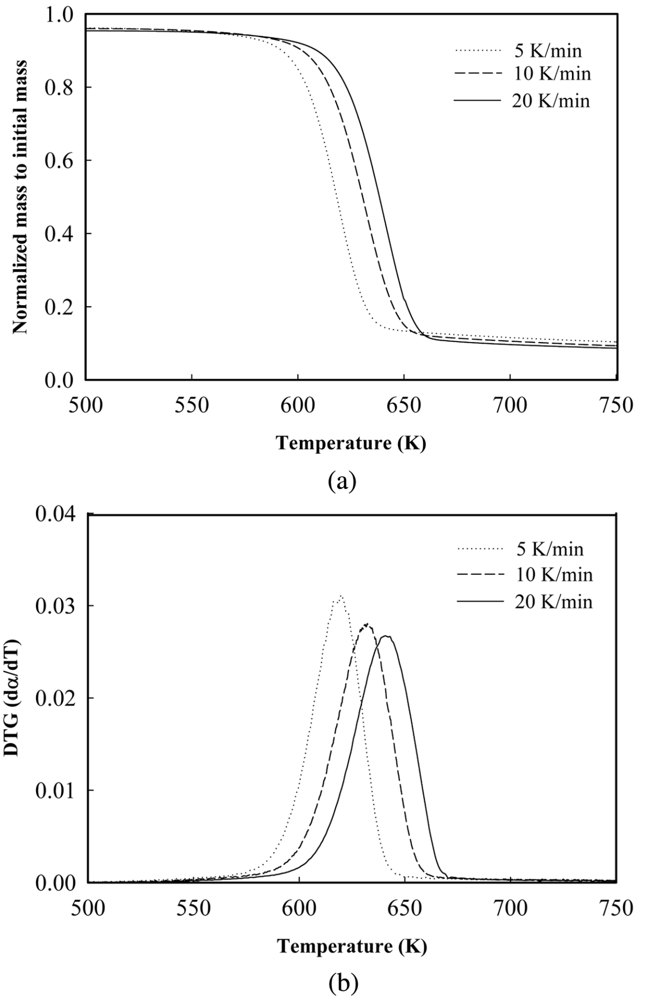
1. Overview of Thermal Decomposition of Cellulose

Fig. 2 illustrates thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) results of cellulose under dynamic conditions. About 10% of the initial weight remains as solid byproducts regardless of heating rate (Fig. 2a). Main decomposition of cellulose is accomplished within a narrow temperature region from 600 to 650 K, implying that the decomposition rate is quite sensitive to temperature.

Fig. 3 displays isothermal kinetic results. The thermal decomposition rates vary significantly with temperature in concordance with the non-isothermal kinetic results. Weight decrease is rarely observed at the initial stage of reaction where the breakdown of cellulose may occur but the molecular sizes of decomposed compounds would be too large to be vaporized. Therefore, the weight decrease is not observed in spite the fact that the cellulose might be actively decomposed [Bradbury et al., 1979]. The higher reaction temperature is able to vaporize fragments of longer chains and also result in faster decomposition, thus leading to a reduction in the retardation period (Fig. 3).

2. Determination of Kinetic Triplet

In order to choose proper reaction model for cellulose, the averaged RTP was constructed from the three RTPs obtained at the isothermal operating temperatures of 633, 638, and 643 K and was compared with the theoretical ones in Table 1. As shown in Fig. 4, the averaged RTP matches excellently with the theoretical one cor-



(a)

(b)

Fig. 2. TGA and DTG thermograms of cellulose under nitrogen atmosphere at the heating rates of 5, 10, and 20 K/min.

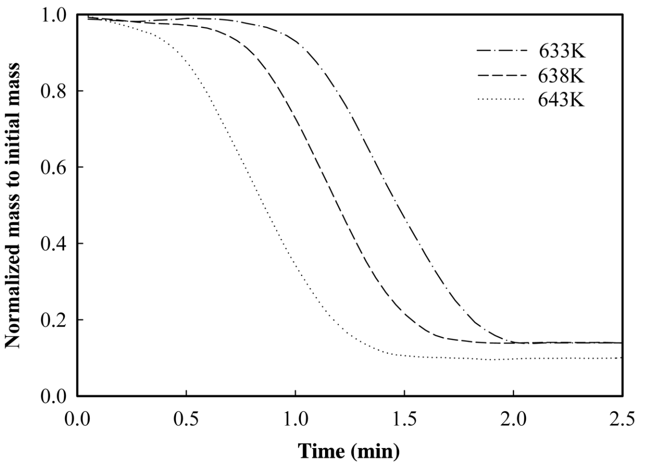


Fig. 3. Pyrolysis kinetic results of cellulose at isothermal operating temperatures of 633, 638, and 643 K.

responding to Avrami-Erofeev function: $g(\alpha)=[-\ln(1-\alpha)]^{1/n}$. The cellulose pyrolysis reaction would be strongly affected by the resistance to mass and heat transfer in cellulose particles [Antal and Varhegyi, 1995; Antal et al., 1998; Blasi, 1996; Liliedahl and Sjostrom 1998; Pyle and Zaror, 1984; Reynols and Burnham, 1997].

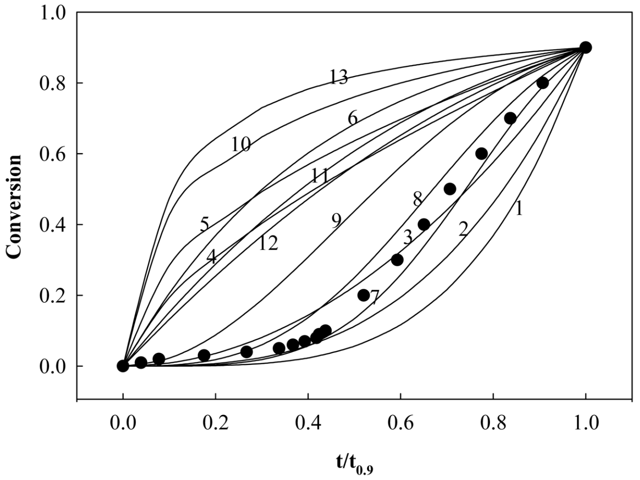


Fig. 4. Comparison of theoretical reduced time plots for reaction models defined in Table 1 with average RTP experimentally determined at three isothermal operating temperatures of 633, 638, and 643 K.

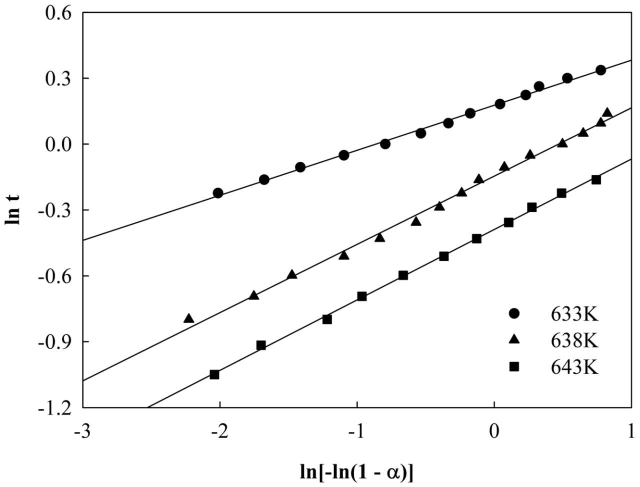


Fig. 5. Plot of lnt for cellulose pyrolysis reaction versus ln(1−α) determined at the isothermal operating temperatures of 633, 638, and 643 K.

To estimate the n values in the $g(\alpha)$ at the isothermal temperatures of 633, 638, and 643 K, taking the natural logarithm of Eq. (3) leads to the following equation:

$$\ln t=\frac{1}{n}\ln[-\ln(1-\alpha)]-\ln k \tag{5}$$

The n value can be obtained from the slope of a plot of lnt versus $\ln(1-\alpha)$, as shown in Fig. 5. The n values at 633, 638, and 643 K, respectively, were estimated to be 2.99, 3.22, and 4.88, leading to the average n value of 3.69. Thus, the $f(\alpha)$ and $g(\alpha)$ for the cellulose pyrolysis reaction with the average n value are denoted to be:

$$f(\alpha)=3.69(1-\alpha)\{-\ln(1-\alpha)\}^{0.73} \tag{6}$$

$$g(\alpha)=[-\ln(1-\alpha)]^{1.37} \tag{7}$$

In addition, the rate constant (k) can be derived from the intercept of a plot of lnt versus $\ln(1-\alpha)$ (Eq. (5)). The k values at the three isothermal operating temperatures of 632, 638, and 643 K were evaluated to be 0.838, 1.157, and 1.479 min^{-1}, respectively. As noted in Fig. 5, high linearities of the plots may support the reliability of the k values as well as the suitability of the reaction model derived here for the cellulose pyrolysis reaction. In line with Eq. (4), the Arrhenius plot of the k values leads to the E and lnA value from the slope and intercept, respectively, to be 192.48 kJ mol^{-1} and 36.41 (A: min^{-1}) with a high linearity ($R^2=0.995$).

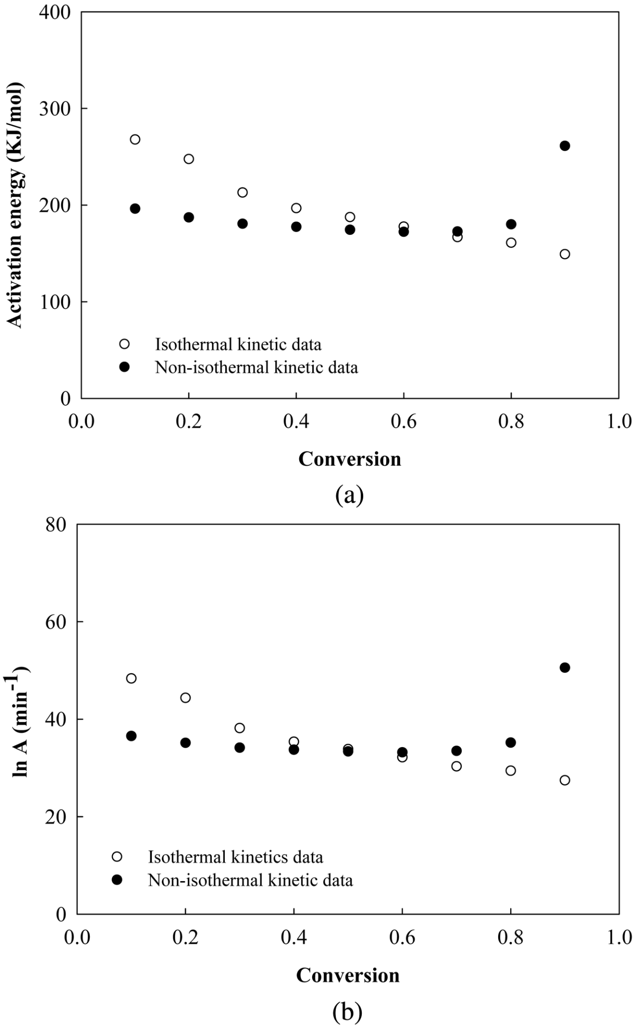
4. Verification of the Kinetic Triplet

For the purpose of verifying the kinetic triplet derived here, the E value was compared with that estimated from model-free methods that are capable of estimating the activation energy without knowing reaction model function. Therefore, the properness of the E value as well as a reaction model function used in the model-fitting method would be assessed indirectly by means of comparing the E value derived from model-fitting method with that from model-free method.

A model-free equation using isothermal kinetic data can be denoted by [Rodante et al., 2002; Tanaka, 1995; Vyazovkin and Wight, 1999]:

$$\ln t_{\alpha,i} = -\ln\left(\frac{A_\alpha}{g(\alpha)}\right) + \left(\frac{E_\alpha}{R}\right)\frac{1}{T_i} \quad (8)$$

Applying the above equation to the isothermal kinetic data, the E value is expressed as a function of α (Fig. 6). The E value decreases slowly with increasing α. The average E value ($0.2<\alpha<0.8$) is estimated to be 192.96±22.15 kJ/mol within a confidence interval of 95%. If the $g(\alpha)$ derived here would be substituted into Eq. (8), the A value is also expressed as a function of α (Fig. 6) and the average of lnA ($0.2<\alpha<0.8$) is determined to be 34.82±3.82 (A: min^{-1}) within a confidence interval of 95%. Since the E and A value derived from the model-free method are quite similar to those from the model-fitting method, the reaction model function determined here would be acceptable to represent the cellulose pyrolysis reaction.



(a)

(b)

Fig. 6. Variation of activation energy and pre-exponential factor with conversion derived from two model-free methods using isothermal and non-isothermal kinetic data.

There is another model-free method that uses non-isothermal kinetic data. The E values derived from the model-fitting method should be in agreement with those from that using isothermal kinetic data despite, using different kinetic data. The Friedman method was introduced as the model-free method by using non-isothermal kinetic data. Thus, comparison of Arrhenius parameters derived from the Friedman method with those estimated here would be useful to verify the validity of the E values as well as the reaction model function. The E values obtained from the Friedman method demonstrate high consistency with respect to α. The average E value within the α range from 0.2 to 0.8 is 177.87±3.95 kJ/mol within a confidence interval of 95%. If the $f(\alpha)$ determined here would be applied to the Friedman equation, the average lnA could be estimated to be 34.70±2.03 (A: min^{-1}) within a confidence interval of 95%. The model-fitting method analyzing isothermal kinetic data shows higher E and A values at the lower α regions (<0.3) where the retardation of thermal decomposition possibly arising from either heat transfer effect or insufficient fragmentation of sample for vaporization or both might be more important role in case of isothermal decomposition reactions. Except for the lower α regions, both model-free methods exhibit high similarities of E and A value, possibly supporting the properness of the reaction model determined here.

Another verification method is to compare theoretical TGA with experimental one. Fig. 7 illustrates the comparison result of theo-

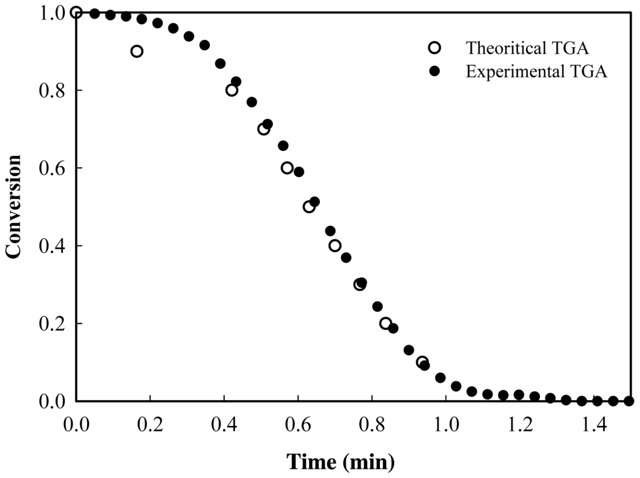


Fig. 7. Comparison of theoretical TGA curve of cellulose with experimental one at an isothermal operating temperature of 643 K.

retical TGA curve derived from applying the derived kinetic triplet with experimental one at an isothermal operating temperature of 643 K. Except for the initial decomposition stages, thermal decomposition curve theoretically derived from the estimated kinetic triplet (E: 192.96 kJ/mol, lnA: 34.82, $f(\alpha)=2.99(1-\alpha)\{-\ln(1-\alpha)\}^{0.67}$) reproduces the experimental one excellently at an isothermal operating temperature of 643 K (Fig. 7). Disparity at the lower α regions may arise from the fact that theoretically estimated thermal decomposition pattern cannot simulate weight decrease at the lower α regions despite of estimating decomposition rate accurately. Weight decrease might rarely occur until reaching fragments of small sizes to be vaporized in spite of active thermal decomposition. Hence, the theoretically estimated thermal prediction cannot duplicate the experimental ones exactly at the lower α regions.

CONCLUSIONS

The reaction model function of cellulose pyrolysis reaction would be accounted for by Avrami-Erofeev function, $n(1-\alpha)\{-\ln(1-\alpha)\}^{1-1/n}$ where n is determined to be 3.69. The activation energy derived from model-free methods exhibits quite similar value to that obtained from model-fitting method adopting the reaction model function of Avrami-Erofeev form. Experimental TGA curve was excellently reproduced by theoretical one derived from applying the derived kinetic triplet under static conditions. Thus, the Arrhenius parameters as well as the reaction model function derived here would be acceptable to represent the cellulose pyrolysis reaction. It is expected that the cellulose pyrolysis reaction would be strongly affected by the resistance to mass and heat transfer in cellulose particles.

ACKNOWLEDGEMENTS

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NOMENCLATURE

A : pre-exponential factor [min^{-1}]
E : activation energy [$\mathrm{J\ mol}^{-1}$]
$\mathbf{g}(\alpha)$: integration from of the reaction model function ($\mathbf{g}(\alpha)=\int_0^{\alpha}[\mathbf{g}(\alpha)]^{-1}\mathbf{d}\alpha$)
$f(\alpha)$: reaction model
k : reaction constant [min^{-1}]
n : reaction order
R : gas constant [$\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$]
t : time [min]
T : temperature [K]

Greek Letter

α : weight conversion at an absolute temperature

Subscript

i : substituting a particular reaction temperature

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