Nonisothermal kinetics of wood degradation in supercritical methanol

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Abstract−The kinetic analysis of wood degradation in supercritical methanol has been studied by a nonisothermal weight loss technique. The weight loss data according to degradation temperature have been analyzed using two integral methods based on Arrhenius form to obtain the kinetic parameters, such as apparent activation energy and overall reaction order. The experiments were carried out for three heating rates of 5.2, 11.6 and 16.3 °C/min. It was found that there are the distinct mass changes over the temperature range of 260-370 °C for all three heating rates, and the weight loss curves were displaced to higher temperatures as increasing of heating rate. The activation energies of wood degradation in supercritical methanol were 73.5-74.5 kJ/mol and 45.2-48.8 kJ/mol, and the reaction orders were 0.59-0.64 and 0.25, depending on the mathematical approach taken in the analysis and the heating rate.

Key words: Kinetic Analysis, Supercritical Methanol, Degradation, Wood

INTRODUCTION

Most of all transportation energy is derived currently from petroleum. The fact that petroleum is nonrenewable is an excellent incentive for developing renewable energy sources. Also, the accelerated rate of growth of energy consumption raises this incentive for all countries. In addition, the burning of fossil fuels, which produces carbon dioxide, has serious environmental consequences. In contrast to fossil fuels, the use of biomass for energy provides significant environmental advantages. Plant growth needed to generate biomass feedstocks removes atmospheric carbon dioxide, which offsets the increase in atmospheric carbon dioxide that results from biomass fuel combustion [1]. Wood and other forms of biomass can be used in various ways to provide energy, such as combustion, gasification, pyrolysis, etc. [2]. Pyrolysis, which converts wastes to fuel or useful hydrocarbons, is a promising and economical process to produce liquid fuels that can be readily stored and transported [3]. But it was never commercialized because of some problems to be tackled such as excessively long degradation time, tar formation and the coking of reactants. These are the reason why new technologies using supercritical fluid are needed in the thermal treatment process of biomass.

Supercritical fluid technology has made enormous progress in the past decade in terms of commercial application and fundamental understanding of solution behavior [4]. Supercritical fluids have distinct properties that may improve many types of chemical process operations. Having the density to liquid, the supercritical fluid has the ability to dissolve many components, whereas the high diffusivity and low viscosity of the supercritical fluid also enable it to behave similar to gas. Such properties of the supercritical fluid tend to maximize the yields of the product in the prescribed reaction time. Thus, they have been used in a variety of polymer process such as

polymerization, extraction, separation, and industrial application [5-7]. Recently, the use of supercritical fluid has been thought to be attractive for chemical conversion of biomass resources [8-11]. Therefore, supercritical water treatment of biomass resources has been studied to convert them to useful chemicals [8,9]. However, hydrolysis products such as glucose were further decomposed rapidly in supercritical water due to its high critical temperature. On the other hand, the critical temperature and pressure of methanol, which are lower than those of water, offer milder conditions for the reaction [12]. Minami and Saka [12] studied the decomposition behaviors of wood biomass in supercritical methanol and reported the methanol with reaction products can be used as liquid fuel because methanol itself is a good fuel.

In this work, the kinetic analysis of wood degradation in supercritical methanol has been studied by a nonisothermal weight loss technique. It is well known that a kinetic investigation is very important to get information for rationally designing the reactor for biomass degradation in supercritical fluids. But unfortunately, such factors as hard reaction conditions, complicated compositions of degradation products, difficulty of continuous operation, etc. tend to limit the kinetic analysis on the degradation of biomass in supercritical fluids. The purpose of this work is to propose a kinetic analysis method of wood degradation in supercritical methanol. The weight loss data according to degradation temperature have been analyzed using two integral methods based on Arrhenius form to obtain the kinetic parameters such as apparent activation energy and overall reaction order.
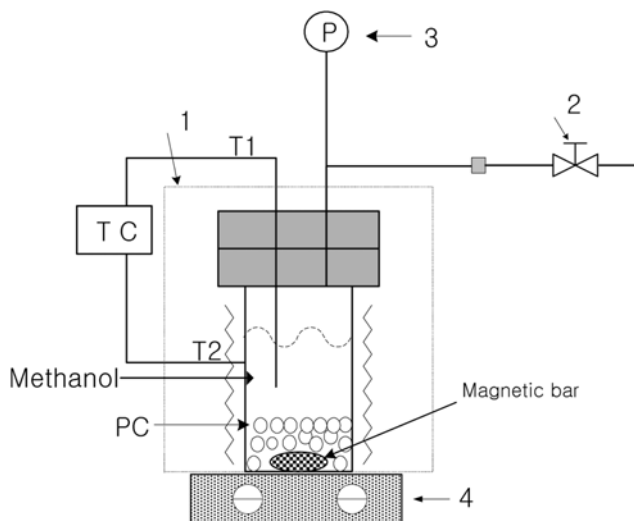
EXPERIMENTAL

The wood chopstick was used as a sample for kinetic analysis in this work. Proximate and elemental analyses of wood sample are shown in Table 1. We can see that the volatile material is the major component of the wood used in this work, and the weight percentages of carbon and oxygen are 52.35 and 39.75%, respectively. Metha-

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Table 1. Proximate and elemental analyses of wood sample

Proximate analysis		Elemental analysis	
Items	Weight fraction (%)	Elements	Weight fraction (%)
Initial moisture	7.78	Carbon	52.35
Volatile matter	78.52	Hydrogen	6.63
Fixed carbon	13.25	Nitrogen	0.16
Ash	0.45	Oxygen	39.75
		Sulfur	0.01

Fig. 1. Schematic diagram of experimental apparatus.
　　1. Autoclave reactor　　4. Hot plate with magnetic stirrer
　　2. Shut-off valve　　　　T1, T2. Termocouple
　　3. Pressure gauge　　　　TC. Temperature controller

nol used as supercritical fluid is a first reagent grade methanol (with at least 99.5% of purity) manufactured by Ducksan Chemical Co., and was used without any further purification. The critical temperature and pressure of methanol were 512.6 K and 8.14 MPa [13]. Fig. 1 shows the schematic diagram of the experimental apparatus used in this work. The stainless steel reactor, whose volume is 25 ml, was fabricated by Parr Instrument Co. The permissible reactor conditions are 500 °C and 55 MPa. Preliminarily, the wood sample was put in a 105 °C oven for a least 24 hr to make the sample dense and dry. At room temperature, a total of 1 g of the wood sample was charged in a stainless steel autoclave with 16 g of methanol. The pressure inside the vessel was monitored by a pressure gauge. The reaction temperature was controlled by PID controller to raise the temperature at the preset temperature with heating rates of 5.2, 11.6 and 16.3 °C/min. During the reaction, the contents in the vessel were agitated by magnetic stirrer to minimize the heat transfer lag. When the reaction temperature reached the preset temperature, the heating of the vessel was interrupted. After the vessel was cooled to room temperature by chiller for rapid cooling, the products were taken out of the vessel. In the nonisothermal weight loss technique proposed in this work, the total conversion of wood degradation with reaction temperature is used for kinetic analysis. Therefore, the fractions of liquid and gas products were not analyzed in this work.

The liquid-solid mixture was filtered on a membrane filter. The solid residue was rinsed with methanol to remove the absorbed liquid organic fraction and weighed after removal of the solvent in dry oven for 24 hours. The conversion α of wood was calculated as follows:

$$\alpha = \frac{W_0 - W}{W_0} \quad (1)$$

where W_0 and W are the initial and final masses of the sample, respectively.

KINETIC MODELS

A kinetic study utilizes the basic rate equation of conversion α for wood degradation, based on Arrhenius forms as:

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(\frac{-E}{RT}\right) \quad (2)$$

where, A, E, T and R are the pre-exponential factor (1/min), the activation energy (J/mol), the temperature of reaction (K), and the gas constant (8.314 J/mol·K), respectively, and n denotes the overall reaction order. If the basic Eq. (2) is taken and a heating rate $\beta = dT/dt$ (K/min) is employed, it can be shown that

$$\frac{d(1-\alpha)}{(1-\alpha)^n} = -\frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \quad (3)$$

Integrating, using the approximation by Horowitz [14], gives

$$\frac{(1-\alpha)^{1-n} - 1}{1-n} = -\frac{ART_s^2}{\beta E} \exp\left[\frac{-E}{RT_s}\left(1 - \frac{\theta}{T_s}\right)\right] \quad (4)$$

In Eq. (4), θ is defined as $T - T_s$, and T_s is the temperature where $d(1-\alpha)/dT$ is maximum or $d^2(1-\alpha)/dT^2 = 0$.
Thus,

$$\left(\frac{d^2(1-\alpha)}{dT^2}\right)_{T=T_s} = -\frac{A}{\beta} n(1-\alpha_s)^{n-1} \frac{d(1-\alpha)}{dT} \exp\left(\frac{-E}{RT_s}\right)$$
$$- \frac{A}{\beta}(1-\alpha_s)^n \exp\left(\frac{-E}{RT_s}\right)\frac{E}{RT_s^2} = 0 \quad (5)$$

Where $1-\alpha_s$ is the weight fraction when $T = T_s$, that is, inflection occurs in weight loss curve. Substituting Eq. (3) for $d(1-\alpha)/dT$ one obtains

$$\frac{E}{RT_s^2} = \frac{A}{\beta} n(1-\alpha_s)^{n-1} \exp\left(\frac{-E}{RT_s}\right) \quad (6)$$

Substituting this expression for RT_s^2 in Eq. (4):

$$\frac{(1-\alpha)^{n-1} - 1}{1-n} = -\frac{1}{n}(1-\alpha_s)^{n-1} \exp\left(\frac{E\theta}{RT_s^2}\right) \quad (7)$$

When $\theta = 0$, $(1-\alpha) = (1-\alpha_s)$ and Eq. (7) yields

$$(1-\alpha_s) = n^{\frac{1}{1-n}} \quad (8)$$

Thus, the weight fraction at which the inflection occurs determines the reaction order, n. Substituting Eq. (8) into (7) one obtains

$$\frac{1 - (1-\alpha)^{n-1}}{1-n} = \exp\left(\frac{E\theta}{RT_s^2}\right) \quad (9)$$

After considering logarithms, the following equations can be obtained:

$$\ln\left[\frac{1-(1-\alpha)^{n-1}}{1-n}\right]=\frac{E}{RT_s^2}\theta \qquad (10)$$

Once n has been estimated by Eq. (8), a plot of

$$Y=\ln\left[\frac{1-(1-\alpha)^{n-1}}{1-n}\right] \text{ vs. } \theta \text{ for n}\neq1 \qquad (11)$$

results in straight lines with slopes to E/RT_s^2. If n=1, Eq. (10) is indeterminate. From the integral approximation and logarithm of Eq. (3), it can be obtained that

$$\ln[-\ln(1-\alpha)]=\frac{E}{RT_s^2}\theta \qquad (12)$$

Thus, a plot of

$$Y=\ln[-\ln(1-\alpha)] \text{ vs. } \theta \text{ for n}=1 \qquad (13)$$

should give a straight line whose slope is E/RT_s^2.

Also from Eq. (3), the following integral expression is obtained:

$$F(\alpha)=\int_0^\alpha\frac{d\alpha}{(1-\alpha)^n}=\frac{A}{\beta}\int_{T_0}^T\exp(-E/RT)dT \qquad (14)$$

After considering integral approximation and logarithm [15], the following equations can be obtained:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \text{ for n}\neq1 \qquad (15)$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \text{ for n}=1 \qquad (16)$$

Thus, plots of

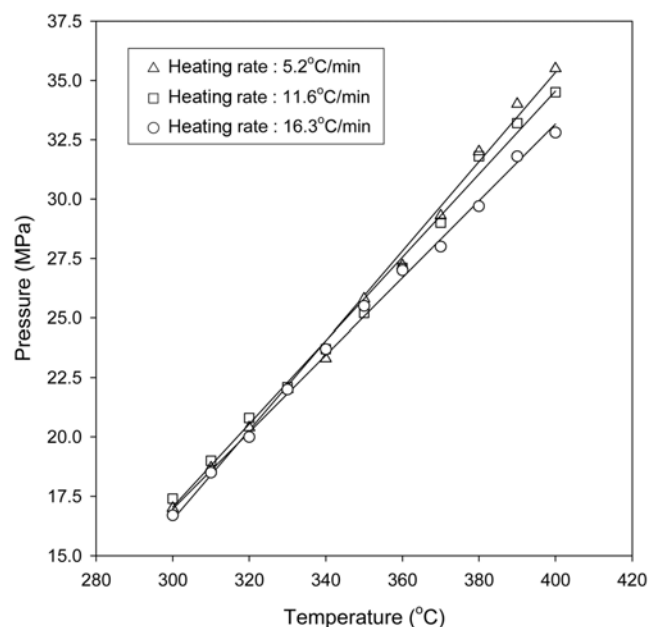$$Y=\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \text{ vs. } \frac{1}{T} \text{ for n}\neq1 \qquad (17)$$

Fig. 2. Pressure according to degradation temperature.

$$Y=\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] \text{ vs. } \frac{1}{T} \text{ for n}=1 \qquad (18)$$

result in straight lines with slopes equal to −E/R for the correctly chosen values of n.

RESULTS AND DISCUSSION

The pressures of each degradation temperature are plotted in Fig. 2. As can be seen, the degradation conditions employed in this work exceeded the critical point of methanol, so the degradation dealt with in this work took place in supercritical methanol. It was also found that the pressures according to degradation temperature are similar between heating rates. The weight loss data of wood degradation in supercritical methanol are shown in Fig. 3. Obviously, it can be seen that there are the distinct mass changes over the temperature range of 260-370 °C for all three heating rates. And it was found that the weight loss curves were displaced to higher temperatures due to the heat transfer lag as increasing of heating rate. At a lower heating rate, the retention time required to reach a given temperature is longer. This would generally result in a higher conversion. Thus, the weight loss curve with a lower heating rate is lower than or leftward to that with a higher heating rate.

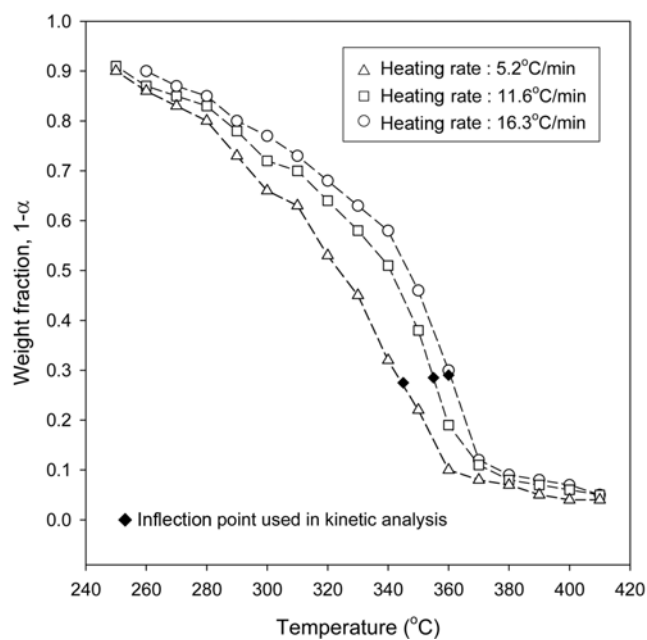The application of Eq. (8) to obtain the reaction order requires

Fig. 3. Weight loss data of wood degradation in supercritical methanol.

Table 2. Weight fraction and temperature at which the inflection occurs in weight loss curve

Heating rates, β (°C/min)	Temperature, T_s (°C)	Weight fraction, $(1-\alpha_s)$
5.2	345	0.275
11.6	355	0.285
16.3	360	0.290

the weight fraction, $1-\alpha_s$ at which the inflection occurs in weight loss curve. However, the weight fraction, $1-\alpha_s$ cannot easily be obtained in the case of wood degradation in supercritical methanol by hard reaction conditions. Therefore, the weight fraction, $1-\alpha_s$ was calculated by interpolation of two points at which the slope of weight loss curve was most steep (Fig. 3). These weight fractions and degradation temperatures at which the inflection occurs are shown in Table 2. From this work, it was obtained that the reaction orders were 0.59, 0.62 and 0.64 for heating rates of 5.2, 11.6 and 16.3 °C/

min, respectively. Fig. 4 shows the plot of Eq. (11) to determine the activation energy. Eq. (10) should also pass through the origin because the intercept of the Y-axis is zero, and the constraint of origin pass was applied to all plots in linear regression. From Fig. 4, it was found that the activation energies of wood degradation in supercritical methanol were 73.7, 73.5 and 74.5 kJ/mol for heating rates of 5.2, 11.6 and 16.3 °C/min, respectively.

Figs. 5-7 show the plots of Eq. (17) or (18) for the application of the kinetic analysis used in this work at heating rates of 5.2, 11.6
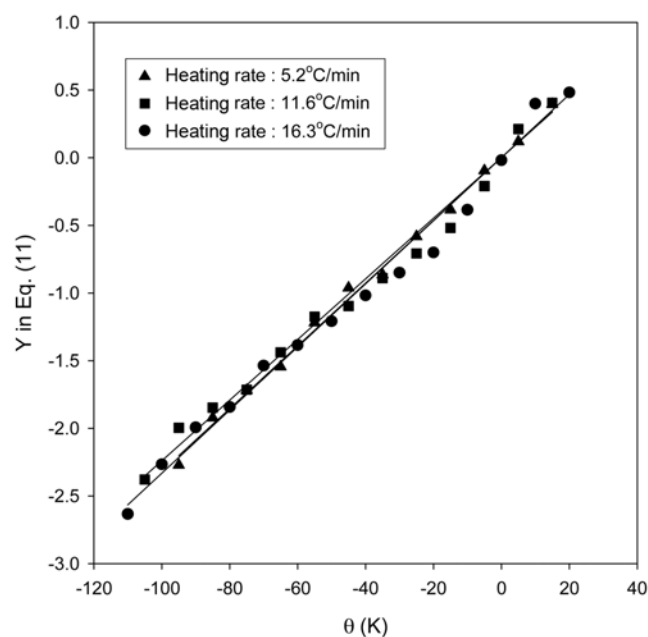

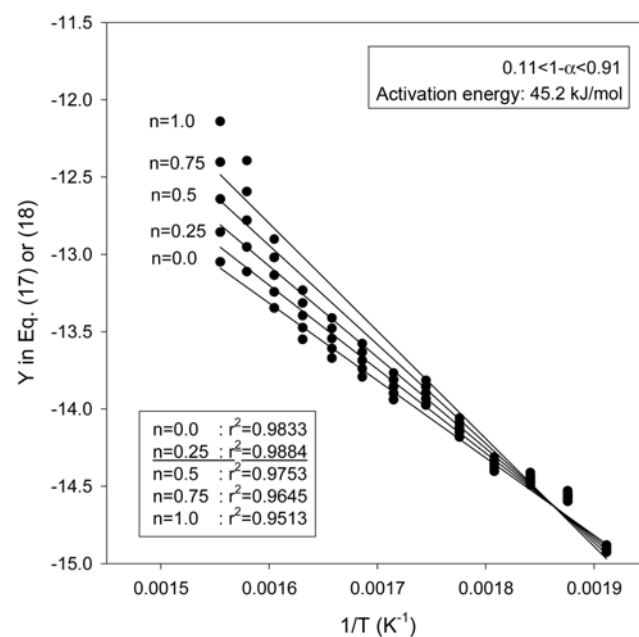Fig. 4. Plots of Eq. (11) for the application of kinetic analysis method.

Fig. 6. Plots of Eq. (17) or (18) for the application of kinetic analysis method at heating rate of 11.6 °C/min.
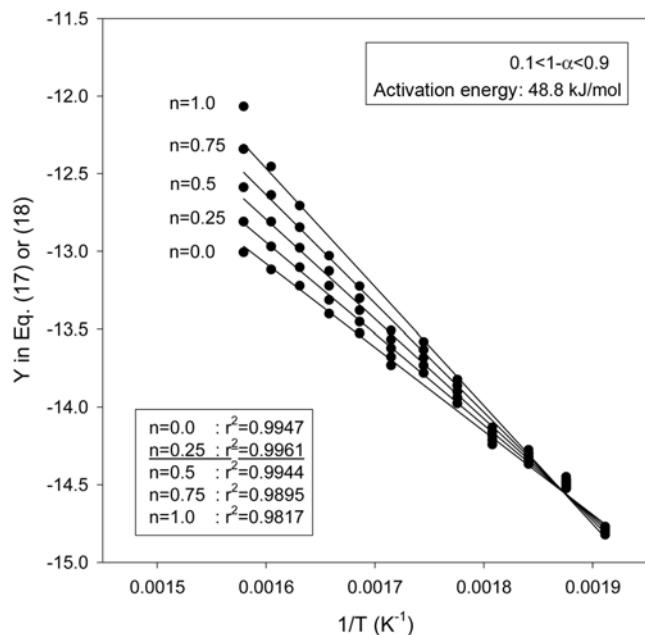

Fig. 5. Plots of Eq. (17) or (18) for the application of kinetic analysis method at heating rate of 5.2 °C/min.
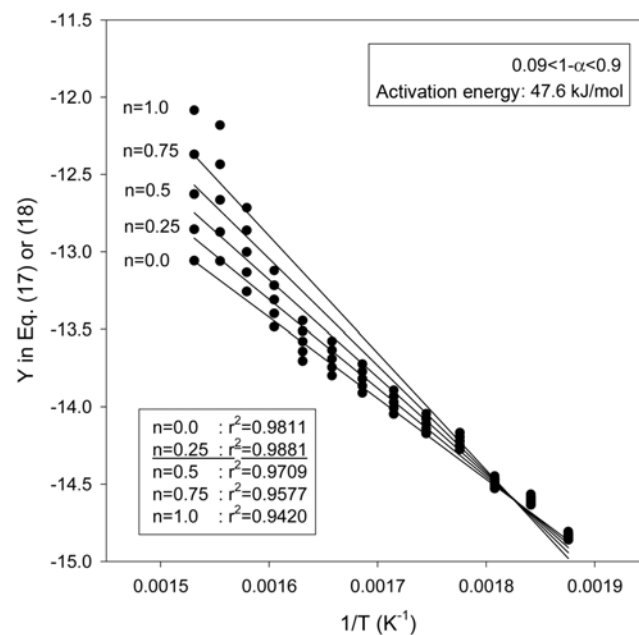

Fig. 7. Plots of Eq. (17) or (18) for the application of kinetic analysis method at heating rate of 16.3 °C/min.

Table 3. Summary of the kinetic parameters obtained in this work

Methods	Heating rates, β (°C/min)	Activation energy, E (kJ/mol)	Reaction order, n
Eq. (8) and (11)	5.2	73.7	0.59
	11.6	73.5	0.62
	16.3	74.5	0.64
Eq. (17)	5.2	48.8	0.25
	11.6	45.2	0.25
	16.3	47.6	0.25

and 16.3 °C/min, respectively. This method has been applied to our data and the best fit values for each heating rate were determined by employing the reaction order values n of 0.0, 0.25, 0.5, 0.75 and 1.0. The best overall fit values were obtained using a value for n= 0.25. And this kinetic analysis method gave apparent activation energies of 48.8, 45.2 and 47.6 kJ/mol for heating rates of 5.2, 11.6 and 16.3 °C/min, respectively.

The kinetic parameters obtained from this work are summarized in Table 3. It can be seen that there were variations in the calculated kinetic parameters depending on the mathematical approach taken in the kinetic analysis. These observations clearly indicate the problems and pitfalls in the selection and utilization of different analytical methods to solve the degradation of wood in supercritical methanol. The use of Eq. (8) requires the weight fraction, $1-\alpha_s$ at which the inflection occurs in the weight loss curve. However, as mentioned above, the weight fraction, $1-\alpha_s$ cannot easily be obtained in the case of wood degradation in supercritical methanol by hard reaction conditions. Therefore, in this work, $1-\alpha_s$ was calculated by interpolation of two points at which the slope of weight loss curve was most steep. Meanwhile, the application of Eq. (17) and (18) only uses experimental data, and therefore this application is capable of providing reasonably reliable.

CONCLUSIONS

The kinetic analysis of wood degradation in supercritical methanol has been studied by a nonisothermal weight loss technique. The weight loss data according to degradation temperature have been analyzed using two integral methods based on Arrhenius form to obtain the kinetic parameters, such as apparent activation energy and overall reaction order. The experiments were carried out for three heating rates of 5.2, 11.6 and 16.3 °C/min. From this work, it was found that there were distinct mass changes over the temperature range of 260-370 °C for all three heating rates, and the weight loss curves were displaced to higher temperatures as increasing of heating rate. The activation energies of wood degradation in supercritical methanol were 73.5-74.5 kJ/mol and 45.2-48.8 kJ/mol, and the reaction orders were 0.59-0.64 and 0.25, depending on the mathematical approach taken in the analysis and the heating rate. It was also found that there were variations in the calculated kinetic parameters depending on the mathematical approach taken in the kinetic analysis. These observations indicate the problems and pitfalls in the selection and utilization of different analytical methods to solve the degradation of wood in supercritical methanol.

REFERENCES

1. D. Mohan, C. U. Pittman and P. H. Steele, *Energy and Fuel*, **20**, 848 (2006).
2. Q. Liu, S. Wang, K. Wang, Z. Luo and K. Chen, *Korean J. Chem. Eng.*, **26**, 548 (2009).
3. S. Kim and Y. Eom, *Korean J. Chem. Eng.*, **23**, 409 (2006).
4. J. Shin, W. Bae, Y.-W. Lee and H. Kim, *Korean J. Chem. Eng.*, **24**, 664 (2007).
5. M. A. Mc Hugh and V. J. Wang, *Supercritical fluid extraction: principles and practice*, 2nd Ed., Butterworth, Boston (1994).
6. L. Benedetti, A. Bertucco and P. Pallado, *Biotechnol. Bioeng.*, **53**, 232 (1997).
7. H.-S. Byun and H.-Y. Lee, *Korean J. Chem. Eng.*, **23**, 1003 (2007).
8. S. Saka and T. Ueno, *Cellulose*, **6**, 177 (1999).
9. M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, **39**, 2883 (2000).
10. S. Saka and D. Kusdiana, *Fuel*, **80**, 225 (2001).
11. G. C. Hwang, J.-H. Choi, S. Y. Bae and H. Kumazawa, *Korean J. Chem. Eng.*, **18**, 854 (2001).
12. E. Minami and S. Saka, *J. Wood Sci.*, **49**, 73 (2003).
13. R. H. Perry, D. W. Green and J. O. Maloney, *Perry's Chemical Engineers' Handbook*, 7th Ed., McGraw-Hill, New York (1997).
14. H. H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
15. A. W. Coats and J. P. Redfern, *Nature*, **201**, 68 (1964).