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# Combustion behavior of *Crymptomeria Japonica* using thermogravimetric analysis method

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***Abstract***

The combustion behavior of *Crymptomeria Japonica* was performed via non-isothermal thermogravimetric method under air atmosphere. The mass loss (TGA) and rate of mass loss (DTG) were measured in terms of time and temperature to estimate kinetic combustion of the biomass. A 10 mg of sample was conducted on heating process from 30 ºC to 850 ºC with four different heating rates of 10, 15, 20, 30 ºC $min^{-1}$ in air flow rate of 20 ml/min. Three main decomposition stages were found including dehydration, active and passive pyrolysis and fix carbon burning. Coats–Redfern method was applied to the TGA data to calculate the kinetic parameters including activation energy, pre-exponential factor, and reaction order. The mass loss curves tend to step to higher temperature range when increases heating rate. The burning rate curves showed the temperature peaks increase in maximum mass loss rate with rising heating rate. The obtained kinetic factors are used to simulate the thermal decomposition and compare with experimental data.

***Keywords****: Crymptomeria Japonica*, thermogravimetric analysis, combustion, thermal decomposition

## 1. Introduction

Biomass is form of the agricultural waste materials can convert to bio-product and biofuels by thermochemical conversion method [1]. The method mainly includes combustion, pyrolysis and gasification. Pyrolysis and gasification mainly produce liquid and gaseous fuels to be processed afterwards from the biomass. Biomass combustion can convert the biomass to heat and power by direct combustion. It can be applied in small-scale applications, domestic stove and in large-scale commercial, heating and electricity production. It also used with coal for co-firing in steam power plants, cement industries, and iron making [2].

Biomass components generally include hemicellulose, cellulose and lignin, and some minor extractives [3]. Volatiles matter of the biomass concerns with hemicellulose and cellulose. Lignin relates mainly to formation of fuel char [1] with low oxidation rate [4].

The decomposition temperature range of hemicellulose, cellulose and lignin are 190-320 °C, 280-400 °C and 320-450 °C respectively. However, some researchers found that decomposition of lignin occurred broadly in temperature range of 200-800 °C [4, 5].

Thermogravimetric analysis (TGA) is a method to investigate and compare the combustion reactivity of various biomasses. TGA and DTG (derivative thermogravimetric) curves are basically used to characterize the devolatilization and combustion behavior of the biomass sample, and corresponding combustion characteristics of fuel like ignition and burnout temperature [6]. During its degradation in TGA, the selected medium such as air, $O_2$, $CO_2$ or their mixture may be used to react with the biomass sample. The results from the thermogravimetric tests give some important kinetic data such as the kinetic constants and the reaction order [6] which are useful for designing combustor [7].

*Cryptomeria Japonica*, also named as Japanese cedar, is one of important trees in Taiwan in terms of economic value [8], growth speed and good wood potential [9]. Since it is very popular in Taiwan, people have considered it as the source of bio energy for a long time. However, poorly carbonaceous properties such as hygroscopic behavior, low grindability, and non-uniform properties due to the diversity of biomass sources [10]. These issues lead to problems in the storage and transport [11, 12].

The aim of this work is to investigate the combustion characteristics of *Crymptomeria Japonica* using thermogravimetric analyzer in non-isothermal condition. Kinetic parameters was obtained by using Coat-Redfern method. The effect of heating rate was also studied.

## 2. Experimental method

### 2.1 Biomass properties

*Cryptomeria japonica* was denoted as CJ in this study. The small pieces of CJ were ground by milling machine to become fine chips. Then the chips were screened by sieve sizing with mesh number of 25. The screened samples are small pieces in length of 0.71 mm. Compositions of CJ samples were analyzed with

Elementar vario EL for ultimate analysis, and Perkinelmer STA6000 Simultaneous Thermal Analyzer for proximate analysis. The results of composition analysis are shown in Table 1.

Table 1 Characteristics of *Cryptomeria Japonica*

| Proximate analysis (wt.%, ar) | | Ultimate analysis (wt.%, dry) | |
|---|---|---|---|
| Moisture | 9.33 | C | 50.63 |
| Volatile matter | 78.13 | H | 6.06 |
| Fixed carbon | 12.11 | N | 0.09 |
| Ash | 0.43 | S | 0.02 |
| HHV (MJ/kg) | 18.60 | O | 43.22 |

**2.2 Thermogravimetric analysis**

The combustion tests were performed by thermogravimetric analyzer, Perkin Elmer STA 6000. The mass loss and rate of mass loss were measured and recorded continuously with Pyris software in terms of time and temperature. Small masses of sample about 10-12 mg with optimal particle size of 0.71 mm (small particle size than 0.71 mm is all sucked during the experiment) was filled in alumina cup. The heating process was conducted in four steps. In the first step, the sample was heated from 30°C to 105°C at a constant heating rate of 20°C/min. In the second step, the temperature was kept at 105°C for 10 minutes to ensure total moisture was released. In the third step, the sample was heated again from 105°C to 850°C at a constant heating rate of 20°C/min to completely pyrolyze the sample. The linear heating rate of 10, 15, 20 and 30 °C/min can be adjusted to study the influence of heating rate. Air was used as the carrier gas with flow rate of 19.8 ml/min.

**2.3 Kinetic study**

The kinetic characteristics of biomass decomposition during the thermogravimetric tests can be modeled with a global kinetic equation as follows:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where $\alpha$ represents the percentage of biomass conversion, $k$ is kinetic constant of the sample and $n$ is the order of reaction. The whole decomposition process can be separated into several stages because the kinetics in each stage is quite different. In the following analysis, $m_i$ denotes the initial mass of CJ sample in the beginning of a stage, $m_f$ denotes the final mass at the end of that stage, and $m_t$ denotes the instantaneous mass during that stage. The definition of $\alpha$ is as follows:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{2}$$

The temperature dependence of the rate constant can be modeled by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \tag{3}$$

where $A$ is pre-exponential factor in 1/s, and $E_a$ is activation energy in kJ/mol.

In a non-isothermal process, the sample was heated with a constant heating rate while the temperature increased linearly. The temperature variation may be represented as the following.

$$\frac{dT}{dt} = \beta \tag{4}$$

Substitution Eq. (3) to Eq. (1) and with some transformations, Eq. (1) can be expressed as follows.

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T_0}^{T} e^{-E_a/RT}\,dT \tag{5}$$

The integral of the left hand side of Eq. (5) can be obtained, and the analytic function depends on the value of $n$. However, the right hand side of Eq. (5) has no analytic solution. The approximated integration method or integral method proposed by Coats and Redfern [13] was adopted in this paper by $2RT/E << 1$ to find the kinetic parameters of the decomposition process. After some transformations, the solution of Eq. (5) becomes the following.

For n = 1,

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \tag{6}$$

For $n \neq 1$,

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \tag{7}$$

Both Eq. (6) and (7) can be represented in a linear form as the following:

$$Y = a + bX \tag{8}$$

where the dependent variable is

$Y = \ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$, for n = 1

$Y = \ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$, for $n \neq 1$

and the independent variable is $X = \frac{1}{T}$ with the coefficients as $a = \ln\left[\frac{AR}{\beta E_a}\right]$ and $b = -\frac{E_a}{R}$

In order to evaluate the kinetic parameters, a proper value of $n$ has to be selected at first. The plot of Y vs. X should show a straight line with high correlation coefficient if a proper value of $n$ is chosen. Linear regression in data analysis function is then used to calculate the values of $E_a$ and $A$ as a and b are determined.

## 3. Results and discussion

**3.1 Combustion characteristics**

Three consequent stages of the combustion process include (1) releasing moisture of the biomass samples, (2) de-volatilization of chemical components, and (3) oxidation of chars [6] when increase temperature shown in Fig.1.

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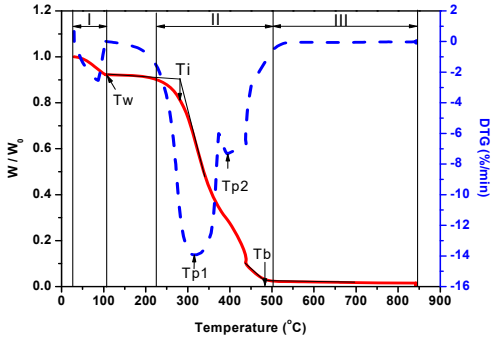


Fig.1 shows the mass loss (TGA) and rate of mass loss (DTG) for heating process of CJ samples with heating rate of 20°C/min in air environment.

Stage I occurs in the temperature range 30.4 °C to 101.6 °C. The moisture of the sample was completely removed, around 9% of mass loss was reduced to dewatering temperature (Tw) of 101 °C.
In range of 101 °C to 238 °C, the mass of sample remains almost the same in this stage.
Stage II shows four important combustion characteristics including ignition, peak 1, peak 2 and burn out temperature. The ignition temperature (Ti) can be considered at the point of intersection of two lines for TGA curve. One is a horizontal line which represent for the amount of fuel moisture loss and a tangent line at the maximum rate of the mass loss [6]. Tp1 is represented by main peak temperature at the maximum mass losing rate (DTG) of biomass components which mainly relate to decomposition of combined hemicellulose and cellulose. Tp2 represents for second peak temperature next to the first peak Tp1 resulting in decomposition of lignin. Another important combustion behavior, the burnout temperature, Tb. It is defined as a horizontal line indicating the amount of fuel ash and a tangent line of the TGA curve showing the rate of lignin volatilization and char oxidation. It can be noted that Tb is the final intersection point in TGA curve which is the boundary temperature of biomass degradation and oxidation [6].
Stage III, there is no mass loss occurs because most of volatiles matter release in previous stage. Residue char can be oxidized without flame in low decomposition rate [6].

### 3.2 Heating rate

In design and operations of combustion system using biomass as fuel, data for each biomass fuel including the influence of heating rate on combustion process is required. It can be seen that as the heating rate increases, the maximum peak (combustion rate) increase significantly, resulting the higher yield of volatile matters in Fig.2 and 3. Fig.2. shows the mass loss curves for CJ at different heating rates. They look very similar, except that the turning point for different stage occurs at different timing. The slower the heating rate is, the later the occurrence of each turning point would be. Rising heating rate leads to shift the mass loss curve towards higher temperature due to shorter time for the samples to reach the temperature.
It is noted in Fig. 3. that increasing heating rate rises mass losing rate and that the peak values of mass losing rate (DTG) in the temperature range of 30-101 °C and 300-360 °C gets higher and higher by increasing the heating rate. The maximum mass losing rate at 20 °C/min heating rate is 1.75 times for that at 10 °C/min heating rate in the same temperature ranges. Besides, the temperature that the maximum mass losing rate occurs steps to higher value which is consistent with mass loss curve in Fig. 2.
It has been reported that too much high heating rate ( > 30 °C/min) lead to insufficient time to transfer heat to the center of the particle and distribute high temperature gradient within the particle [14]. Too much low heating rate will take longer time in the experiment. Thus, the moderate heating rate of 20 °C/min represents the reasonable choice to study the kinetic paraneters. It is also confirmed that the heating rate shows better reactivity of the wood as the temperature gradient with the particle is more uniform [14].
Table 2 showed the effect of heating rates on combustion characteristics of the CJ. When heating process increased, the thermal degradation processed was delayed. Rising heating rates indicates that the sample reach to the temperature in a shorter time, so the ignition, peak and burnout temperatures were shifted to higher temperature.

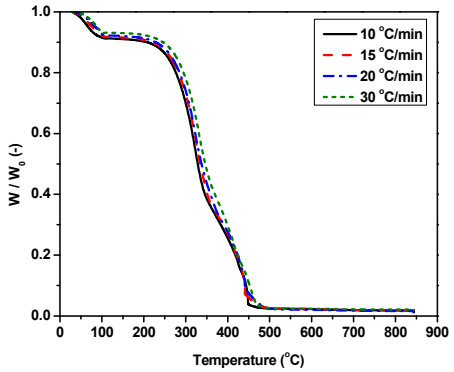


Fig.2 mass loss of CJ at different heating rate

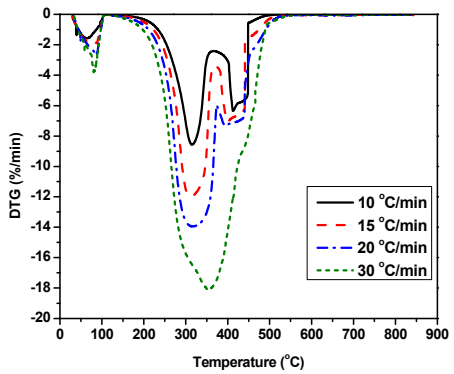


Fig.3 rate of mass loss of CJ at different heating rate

Table 2 Temperature on heating rate

| Combustion Parameter | Heating rate (°C/min) | | | |
|---|---|---|---|---|
| | 10 | 15 | 20 | 30 |
| Dewatering | 112 | 107 | 107 | 106 |
| Ignition | 266 | 280 | 282 | 285 |
| Peak 1 | 315 | 312 | 315 | 352 |
| Peak 2 | 413 | 399 | 393 | - |
| Burnout | 449 | 446 | 448 | 478 |

### 3.3 Kinetic analysis

Table 3 shows the kinetic parameters ($E_a$, $A$, and $n$) of CJ, which can be used for predicting mass loss of the biomass by Eq. (2). The kinetic parameters can be divided into 3 different stages. The higher value for $E_a$ was found by stage II due to decomposition of hemicellulose-cellulose. The lower values $E_a$ occurred in stage III due to decomposition of lignin and oxidation of char.

Table 3 kinetic parameters of CJ from TGA

| Kinetic factor | Temperature range, °C | | | |
|---|---|---|---|---|
| | 31-104 | 233-373 | 377-495 | 500-832 |
| $E_a$ (kJ/mol) | 67.14 | 102.63 | 157.4 | 51.26 |
| $A$ (1/min) | $1.7\times10^{8}$ | $8.5\times10^{6}$ | $4.3\times10^{9}$ | 2.02 |
| n | 1 | 1 | 1 | 1 |
| $R^2$ | 0.98 | 0.98 | 0.98 | 0.97 |

Fig.4 shows comparison of simulated and experimental results of CJ in air environment at 20 °C/min. It can be seen that the calculated mass loss curve fits the measured data very well in the first stage. However, the shape of the predicted curve does not fit the measured data quite well in the second and third stage. The predicted mass loss is slower than the measured rate for second and third stage. As a result, the predicted time duration of gasification is longer than the measured data in the two stage. These may cause from volatile matter in cellulose and lignin are expelled quite fast. However, our reaction order (n=1) is not fit with the phenomena. It may use reaction order that is higher than 1 to fit the experiment curve.

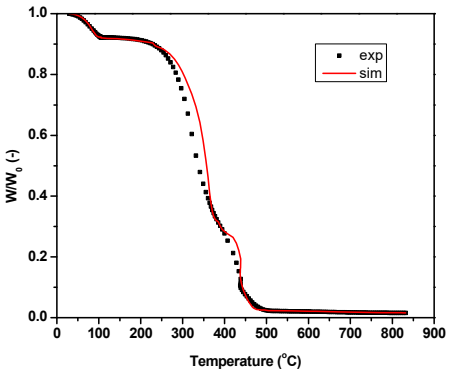


Fig.4 compare simulated and experimental results of CJ in air at 20 °C/min

## 4. Conclusions

The combustion characteristics of *Cryptomeria japonica* were analyzed by TGA in air environment at various heating rate of 10, 15, 20 and 30 °C/min with mean particle size of 0.71 mm. Three stages of decomposition of CJ were found including dewatering, hemicellulose-cellulose decomposition and lignin decomposition and char oxidation.
The main degradation is the second stage which relate to decompose of hemicellulose and cellulose. The ignition and burn out temperature were found in range of 266-285 °C and 446-478 °C respectively. Increasing heating rate lead to the mass loss step to higher temperature range. The peak of the rate of mass loss also increase with heating rate.

## 5. Acknowledgement

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