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## A thermogravimetric analysis of lignin char combustion

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### Abstract

Understanding the combustion behavior is the basic requirement for a new resource to be used as an alternative fuel for the industrial design of the future plants. In this article, thermogravimetric analysis (TGA) of lignin char combustion in different heating rates (5, 10 and 15 °C/min) was investigated. Extracted combustion indices showed increased weight loss rate, peak temperature and burnout temperature but no change in ignition temperature for all samples when the heating rate increased. Lignin chars containing higher volatile material illustrated higher combustibility through the low ignition and burnout temperatures. Kinetic parameters of lignin combustion were also obtained by the Coat-Redfern method in the first-order kinetic model. High combustibility of high volatile sample (L300: vol%=41) was also confirmed by its low activation energy which was 46.68 compared to 150.34 for L500 (vol%=18) and 174.37 kJ/mol for L650 (vol%=5.1). The pre-exponential factor was also measured to be 2.61E-01, 8.15E+06 and 1.21E+08 min<sup>-1</sup> for L300, L500 and L650 respectively.

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*Keywords:* Lignin char; combustion; heating rate; kinetics

### 1. Introduction

Biomass-based renewable resources which are carbon-neutral and low-emission fuels, has gained many attentions in the gradual substitution of conventional fossils fuels [1,2]. The inferior properties of biomass such as high moisture content, low volumetric energy density and low grindability made the costs in fuel transportation storage and processing to be high, inhibit biomass market promotion, especially in combustion applications [3,4]. Pre-treatment methods such as pyrolysis (torrefaction and carbonization) that convert biomass residues to the biomass char can achieve high-quality biofuels. Pyrolysis can improve combustion, calorific value and fixed carbon content and these

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all will be surpassed by increased pyrolysis temperature [5]. For biomass utilization in applications such as boilers, powder generation or blast furnace injection, combustion behavior is of a great importance. Hence, a deep knowledge of the thermal behavior of biomass is critical to assess the feasibility, design and scaling of industrial biomass conversion applications [6,7]. Kinetic parameters obtained by kinetic analysis of biochar combustion data is a good measure of the biochar combustibility and reactivity [8]. In addition, obtained information is important for the design and control of processes aimed to use biochars [9]. Combustion properties of a wide range of biomass fuels have been studied with thermogravimetric methods in several publications with a focus on different parameters as well as heating rate [14–18]. Results show that peak and burnout temperatures of biomass samples shift to the higher temperature intervals as the heating rate increases [6,8].

Although several studies pointed out combustion properties of bio-based fuels, there is limited information regarding lignin chars. Lignin chars are the solid product of slow pyrolysis of lignin, a by-product from bio-ethanol production with enzyme hydrolysis and yeast fermentation. The considerable amount of produced lignin in this process was used for the steam production for bioethanol plant and for heat and electricity generation. Nowadays, lignin is going to be considered as an option for coal replacement in iron and steel production. This new application arose a need for more data related to pyrolysis and combustion of lignin.

In the present study, the combustion behavior of three lignin chars are investigated with thermogravimetric analysis (TGA), and the characteristics of the thermal degradation of the lignin chars at different heating rates are studied. In addition, kinetics of lignin char combustion via Coat-Redfern isoconversional method (CR) is investigated and kinetic parameters are extracted. This research has provided a good reference for lignin char combustion.

## 2. Materials and methods

### 2.1. Materials

In this study, we used lignin char. The by-product lignin samples from St1 Renewable Energy Oy. bio-ethanol production plant pyrolyzed in a slow pyrolysis chamber in University of Oulu, Finland. Lignin chars were obtained from pyrolysis with a heating rate of 5 °C/min and the final temperature of 300, 500 and 650 °C (LX, L=lignin X pyrolysis temperature). Proximate analysis (ash, volatile matter, moisture) and ultimate analysis (C, H, N, S, O) of lignin chars are reported in Table 1. For the combustion tests, lignin chars were crushed and ground by a lab-scale centrifugal mill (Netzsch ZM200). The mean particle size of the pulverized lignin chars was around 55, 54 and 59 microns for L300, L500 and L650 respectively.

Table 1 Proximate, ultimate analysis of the samples

samples	Proximate analysis (wt%, db)			Ultimate analysis (wt%, db)				
	VM	Ash	FC	C	H	N	S	O
L300	41.0	0.5	59.2	75.3	5.14	0.97	0.101	18.0
L500	18	0.7	83	85.9	3.56	1.23	0.121	8.6
L650	5.1	0.9	94.0	93.7	2.05	1.33	0.115	1.9

VM: volatile materials, db: dry basis, FC: fixed carbon

### 2.2. Combustion experiment- thermal gravimetry analysis

Combustion of lignin chars was examined with a thermoanalyzer Netzsch STA 449 F3 Jupiter. Around 5 mg of powdered samples inside an alumina dish crucible (17 mm diameter) heated from 20 to 1000 °C at three heating rates of 5, 10 and 15°C/min and a flow rate of 50 mL/min air. Combustion indices: DTG peak temperatures, the maximum rate of weight loss (Rmax, %/min), initial temperature (Ti) and burn out temperature (BOT) were determined for each sample. Ti is defined as the temperature, in which the derivative of the weight loss curve (DTG) first reaches the value

of 1 %/min. Rmax, %/min is the maximum reactivity defined from the DTG curve. BOT is the temperature at which the weight loss reaches the 1 %/min at the terminal phase of DTG profile. All experiments repeated to assure the repeatability of the data.

### 2.3. Kinetic study

Kinetic equation for solid-state reactions can be expressed based on conversion rate as follows:

$$d\alpha/dt=k(T)f(\alpha) \quad (1)$$

where  $\alpha$  is the conversion degree during pyrolysis,  $k(T)$  is the reaction rate constant which can be explained by the Arrhenius law and  $f(\alpha)$  is the function of the reaction mechanism. Whereby,  $\alpha$  and  $k(T)$  can be calculated with Eqs. (2) and (3), respectively.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where  $m_0$ ,  $m_t$  and  $m_\infty$  refer to the sample mass at the initial time,  $t$  and the end of the experiment, respectively.  $A$  is the pre-exponential factor and  $E_a$  is the activation energy of the reaction.  $R$  is the universal gas constant, and  $T$  is the reaction absolute temperature. Considering a linear heating rate,  $\beta = dT/dt$ , Eq. (1) can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

The integration function of conversion is expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (5)$$

In this integral expression,  $T_0$  is the initial absolute temperature. This is a basic equation that enables determination of kinetic mechanisms in non-isothermal solid thermal degradation reactions [10]. Kinetics parameters can be obtained from non-isothermal rate laws by both model-fitting and isoconversional (model-free) methods [10–13].

Model-fitting methods involve fitting different models to  $\alpha$ -temperature curves and simultaneously determining the activation energy ( $E$ ) and pre-exponential ( $A$ ).

There are several non-isothermal model-fitting methods. One of the most common models being the Coats-Redfern (CR) method [14,15]. This method utilizes the asymptotic series expansion for approximating the exponential integral in eq. (5) giving:

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

where  $\bar{T}$  is the mean experimental temperature. The form of  $g(\alpha)$  that gives a straight line with the highest correlation coefficient will be considered the function of the model that best represents the kinetics of mass loss for each separate reaction.

The plot of the left-hand side of eq. (6), which contains the model  $g(\alpha)$  versus  $1/T$  gives  $E_a$  and  $A$  from the slope and intercept respectively.

### 3. Results and discussion

### 3.1. Thermal characteristics of biochars

Combustion characteristic of lignin chars at different heating rates was investigated using TGA. Results are depicted in Fig. 1. In addition, Fig. 2 compares combustion indices of different biochars in three heating rates. The results reveal higher combustibility of L300 which is clear based on its low  $T_i$ , DTG peak and BOT temperatures. This early ignition of biomass is a key factor in the earlier completion of volatile combustion and the consequential improvement in particle burnout [16]. In general, TG-DTG graphs of combustion of a dry sample represent two weight loss stages. In the first stage, decomposition of biomass components (hemicellulose, cellulose and lignin) take place and the next stage is the combustion of complex and thermally stable structure [17–20]. Among the three samples studied in present research, only L300 char depicted two distinguished stages of combustion in each heating rate. One in 250–420 °C and the other in the range of 420–550 °C.

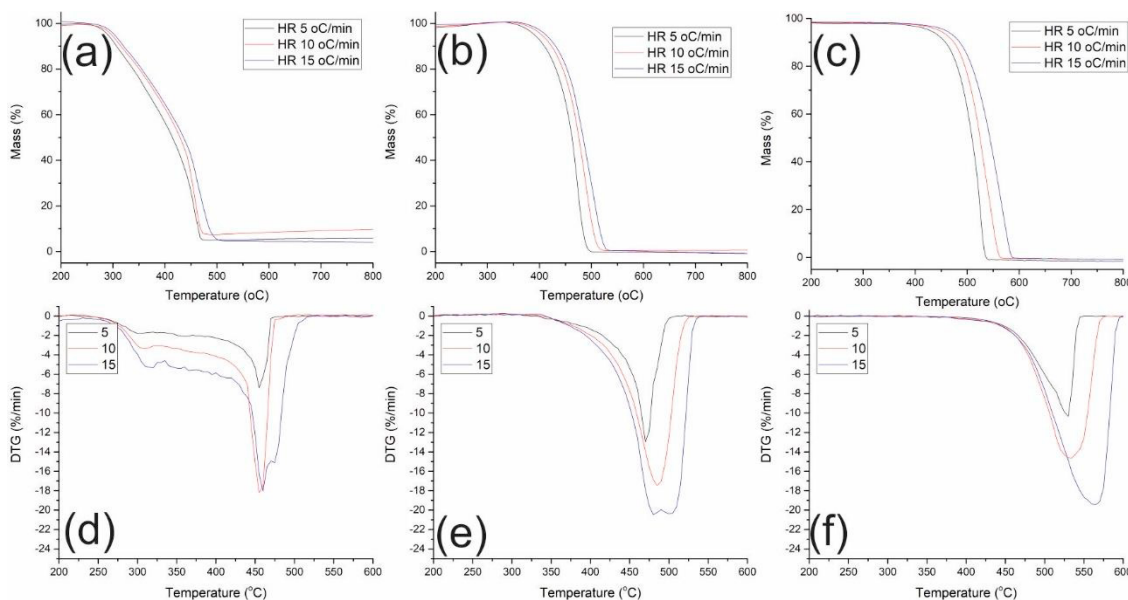


Fig. 1. TGA-DTG graphs of combustion in 5 (black), 10 (red) and 15 (blue) °C/min heating rates. (a,d) L300 (b,e) L500, (c,f) L650.

In fact, it is an effect of the volatile combustion and pyrolysis of the high volatile L300 sample [21]. The release of volatile materials enhances the devolatilization and combustion of the rest of the material. L500 and L650 with less volatile materials showed almost one combustion stage with combustion as the main reaction. Also, it can be seen from weight loss curves that all samples contained quite a small amount of ash that leads to a complete combustion with almost 100% weight loss up to the end of the experiment.

The weight loss curves of the samples depicted no change in the temperature of starting the reactions ( $T_i$ ) at different heating rates. This implies that at the beginning of the combustion process, the heating rate is not the dominant factor. For the higher heating rates, a sharper drop in DTG graphs to the higher weight loss rates observed with a small peak shift to higher temperatures. The weight losses of all samples are faster at higher heating rates. Higher heating rates also delayed the BOT and shifted it to higher temperatures. It means that the combustion of lignin chars in higher heating rates has occurred in a wider temperature range.

The reason is that at lower heating rates, the heating of biomass particles occurs more gradually leading to a more effective heat transfer to the material bed and between particles. By increasing the heating rate, the heat transfer would

not be as efficient as it was at lower heating rates. Therefore, more time or higher thermal gradient will be required to complete the combustion reactions [6,8,22,23].

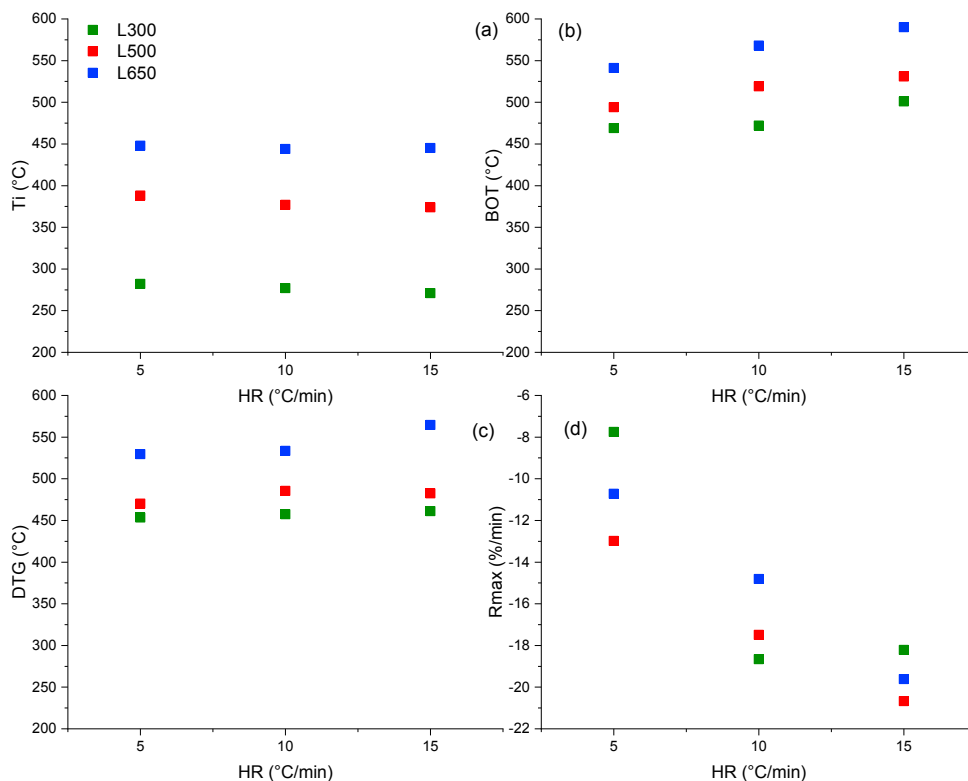


Fig. 2. Effect of heating rate on combustion indices of lignin chars (a)  $T_i$ , (b) BOT, (c) DTG and (d)  $R_{max}$ .

### 3.2. Reaction kinetics

Kinetic parameters of lignin chars were calculated using CR (Eq. 6) method and first-order reaction model which is a good fit for solid-state combustion reactions [11,24,25]. High correlation coefficient ( $R^2$ ) values reported for the fitted models indicated the satisfactory model fitting of experimental data. Measured activation energies for lignin chars in CR model were in the range of 45-198 kJmol<sup>-1</sup> and in agreement with activation energies reported in many biomass combustion studies like 40-165 kJ mol<sup>-1</sup> for Miscanthus plant char [26] and 97-240 for pine and coal blends [24].

The activation energy of combustion reaction can be used to describe the reactivity of coal and chars as it is the required energy to start the combustion reaction. L300 is highly reactive to oxygen with the lowest activation energy while L650 has the highest activation energy. The volatile material content of char which can facilitate combustion reactions becomes successively lower as the pyrolysis temperature increase (indicated in Table 2) is the reason for higher reactivity of L300 compared to L500 and L650. Combustibility (reactivity to air) is higher in biochars pyrolyzed in lower temperatures. In fact, the increased structural ordering of the carbon matrix with temperature and lowering the concentration of reaction sites is the reason for lower reactivity and higher activation energy in chars which pyrolyzed in higher temperatures [16]. Furthermore, increasing the heating rate had a negligible effect on activation

energy of lignin combustion. This confirms our observations of  $T_i$  which wasn't affected by heating rates in all three lignin samples.

Table 2 Kinetic parameters of lignin char combustion obtained by CR method.

Heating rate	L300			L500			L650		
	E (kJ/mol)	A (min <sup>-1</sup> )	R2	E (kJ/mol)	A (min <sup>-1</sup> )	R2	E (kJ/mol)	A (min <sup>-1</sup> )	R2
5	46.01	1.35E-01	0.9923	146.26	2.81E+06	0.9884	178.26	9.97E+07	0.9910
10	46.85	2.63E-01	0.9825	154.37	1.39E+07	0.9946	183.61	2.58E+08	0.9978
15	47.19	3.86E-01	0.9843	150.37	7.79E+06	0.9986	161.24	6.35E+06	0.9988
Average	46.68	2.61E-01		150.34	8.15E+06		174.37	1.21E+08	

E: activation energy (kJ/mol), R2: correlation coefficient, A: (pre-exponential factor).

#### 4. Conclusion

The combustion characteristic and kinetic behavior of the lignin char were studied by using a thermogravimetric analyzer at three heating rates (5, 10, 15 °C/min). The results showed an increase in DTG peak and burnout temperature of lignin chars by increasing the heating rate which assumed to be related to heat transfer limitations. Furthermore, volatile content played a significant role in increasing the combustibility of lignin chars by decreasing ignition and burnout temperature. The CR method, a commonly used isoconversional method, was applied to estimate the activation energy based on first-order reaction model. The activation energy for combustion of L300, L500 and L650 samples was 46.68, 150.34 and 174.37 kJ mol<sup>-1</sup> respectively. The pre-exponential factor was also obtained as follows: A = 2.61E-01, 8.15E+06 and 1.21E+08 min<sup>-1</sup> respectively for L300, L500 and L650.

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