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Research Paper

Thermal degradation kinetics of sawdust under intermediate heating rates

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HIGHLIGHTS

- TGA of biomass at intermediate heating rates of 140–200 °C/min.
- Thermal degradation of hardwood sawdust studied using KAS and FWO models.
- Kinetic parameters were obtained for pyrolysis and oxycombustion.
- The average activation energy dependent on conversion and heating rate.

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ABSTRACT

In this work, thermal degradation behavior of sawdust under N_2 and O_2 environments were investigated to derive the kinetics parameters. Thermogravimetric analysis was carried out at various intermediate heating rates (140–200 °C/min). Kinetic parameters were calculated using Kissinger–Akahira–Sunose and Flynn–Wall–Ozawa models. It was found that the activation energy of both pyrolysis and oxycombustion were different from previous studies. Higher heating rate affected not only the temperature at maximum weight loss, but also the apparent activation energy in any conversions of biomass due to pyrolysis and oxycombustion. Activation energy of sawdust pyrolysis appeared to peak around 40–50% conversions while oxycombustion did around 15–25%. The activation energy was found to be in the range between 35–110 kJ/mol and 35–129 kJ/mol for pyrolysis and oxycombustion, respectively.

1. Introduction

Common sources of biomass to produce bio energy include several kinds of wood, bark, agricultural crops, nuts and seeds, cellulose and lignin, and natural fibers [1,2]. One of those feeds is sawdust which was the subject of this work. Wood, articles of wood and wood furniture industry of Thailand was one of the major export earners, about 2500 million USD per year. There were six types of wood factory in Thailand; solid woods, solid laminated wood panels, plywoods, veneers, particle boards, fiber boards. There are plenty of wood residues in terms of sawdust. Sawdust is identified to have great potential to be a major renewable energy resource for Thailand [3,4]. It may be used to produce bio-oil [5,6].

Pyrolysis and combustion are thermal decomposition processes caused by heat. Due to the complexity of thermal decomposition reactions of natural fibers, extensive researches have been carried out in determining individual behaviors of the main components of biomass [7]. Basic process kinetics of the biomass are useful for further analysis and better understanding of the bio energy production behavior. Thermo gravimetric analysis (TGA) is the most common technique used for kinetic analysis of devolatilization and combustion processes to obtain parameters such as activation energy (E_a), and reaction order. The approach allows obtaining the dependence of the kinetic parameters with the conversion from thermogravimetric (TG) and differential thermogravimetric (DTG) curves measured at different heating rates, without making any assumptions about the reaction function and reaction order.

High heating rate is one of the key factors to produce high yield of bio-oil. Most TGA studies reported so far focus on low heating rates (about 5–80 °C/min) [8–15]. Xu et al. [16] studies pyrolysis kinetic characteristics of sawdust samples at heating rates of 30, 40, and 50 °C/min by TGA with at nitrogen feed. The result showed that heating rate has influence on the decomposition processes. Increasing the heating rate appeared to increase the start and end temperatures of each stage of reaction. Slopiecka et al. [15] preformed TGA on hardwood sawdust at higher heating rate of 20, 40, and 80 °C/min. TGA curves lateral shift to higher

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temperature of thermal degradation as the heating rate was increased [12]. Higher heating rates causes biomass not only to be degraded in a narrow temperature range but also increased the max peak rate. To apply the higher heating rate application in TGA, equilibrate method segment which is very repeatable and achieves rates was required. A lack of literature data exists concerning the combustion of wood in fast pyrolysis condition, especially at high (500–1000 °C/min) and intermediate heating rates (100–500 °C/min). It was known that heating rates in the TGA experiments influence the characteristics of TG curves [17]. The research findings showed that higher heating rates affected weight loss rate in such a way that time taken to reach the pyrolysis temperature was shorter and the inner part of particles underwent pyrolysis at the temperature at which the maximum weight loss rate moved to higher zone [12]. However, reaching heating rates at the order of 1000 °C/min in TGA under laboratory condition is considered extremely difficult [18]. The porosity and surface area of lignite, which perhaps can be best compared to wood, were only slightly enlarged when the heating rate was increased from 0.1 to 1000 °C/s. It was concluded that the surface area was not so much affected by the heating rate or pyrolysis temperature [19]. Relatively high heating rates in the range of 100–400 °C/min would be more realistic to explain the behavior of pyrolysis. The reaction time is decreased by nearly an order of magnitude upon changing the heating rate from 1 to 300 °C/s. In this work, intermediate heating rates between 140 and 200 °C/min are of interest that may give some insight into thermal decomposition experienced by reactions occurred to biomass during fast pyrolysis.

Isoconversional models can follow either a differential or an integral approach to the treatment of TGA data. They are considered as a helpful solution for truly determining activation energy [16]. In this work, Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) model-free methods were chosen. They were founded on an isoconversional basis where in the degree of conversion, x, for a reaction is assumed to be constant and therefore the reaction rate, k, depends exclusively on the reaction temperature [19]. The advantage of the model-free analysis is founded on its simplicity and on the avoidance of errors connected with the choice of a kinetic model [20].

The objectives of this study are therefore to investigate the effect of intermediate heating rates in TGA on thermal degradation kinetics of sawdust, and to establish their kinetic parameters values through a dynamic thermogravimetric analysis by model-free methods. This study focuses on heating rates of 140–200 °C/min. Both pyrolysis and combustion are carried out to determine their activation energy using KAS and FWO models.

2. Materials and methods

2.1. Sample preparation

Sawdust in this work was obtained from furniture industry in Phrae Province. It was derived from the raw materials of recent plant main kinds of hardwood. Hard woods that used were Teak (*Tectona grandis*), *Afzelia xylocarpa*, and *Dalbergia oliveri*. They were air dried naturally in a room at ambient condition. The samples were milled and sieved through a 120 mesh screen (with sieve size of 0.125 mm.) and were sorted to separate adhesives and other impurities visually and manually, prior to analyses and the TGA test runs. Bomb calorimeter was used to evaluate for gross heating value. Moisture, volatile matter, fixed carbon and ash and CHNS-O were also analyzed, following ASTM standards. All analyses were undertaken at the Scientific Equipment Center, Prince of Songkla University, Thailand. Proximate and ultimate analysis results of the sawdust are shown in Table 1.

Table 1
Analysis of industrial sawdust samples.

Properties	Biomass Sawdust
Ultimate analysis	
C (dry basis wt%)	44.95
H (dry basis wt%)	6.71
O (dry basis wt%)	24.23
N (dry basis wt%)	0.16
S (dry basis wt%)	n/a
Proximate analysis	
Moisture content (wt%)	7.68
Volatile fraction (wt%)	73.65
Fixed Carbon (wt%)	16.18
Ash content (wt%)	2.49
HHV (MJ/kg)	16.37

2.2. TGA experiments

The experiments were performed using a Mettler Toledo, thermogravimetric analyzer model, TGA/SDTA 851 at the National Metal and Materials Technology Center, Ministry of Science and Technology. Both research grade high purity nitrogen and oxygen were used as the carrier gases to maintain pyrolysis and combustion conditions, respectively. Oxycombustion was of interest because it has significant advantages as cost effective without the need to reduce CO_2 emissions. The volume flow of N_2 and O_2 were 50 ml/min. TGA were performed at four different heating rates; 140, 160, 180 and 200 °C/min, with an initial sample mass of about 3 mg. The sample was then heated constantly from room temperature to 800 °C. The continuous records of weight loss and temperatures were obtained. At least three runs were performed for each condition.

Mass transfer resistance was reduced as much as possible by working with high gas flows and small sample mass in the TGA experiments. The particle size ranged from 80 to 120 meshes, indicating that the internal mass transfer resistance could be ignored [21,22].

2.3. Kinetic analysis

The fundamental rate equation used in all kinetic studies is generally described as

$$d\alpha/dt = kf(\alpha) \tag{1}$$

where k is the rate constant and $f(\alpha)$ is the reaction model, a function depending on the actual reaction mechanism. Eq. (1) expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the reactant concentration loss and rate constant [22].

The results of thermogravimetric experiments are expressed as a function of conversion α, which was defined as follows:

$$\alpha = (W_0 - W_t)/(W_0 - W_\infty) \tag{2}$$

where W_0 is the initial mass of the sample, W_t is the mass of the sample at time, and W_∞ is the final residual mass.

$$k = A\exp(-E/RT) \tag{3}$$

where E is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/K mol), A is the pre-exponential factor (1/min), T is the absolute temperature (K). The combination of Eqs. (1) and (3) gives the following relationship:

$$d\alpha/dt = A\exp(-E/RT)f(\alpha) \tag{4}$$

For a dynamic TGA process, introducing the heating rate, $\beta = dT/dt$, into Eqs. (4) and (5) is obtained as:

$$d\alpha/dT = (A/\beta)\exp(-E/RT)f(\alpha) \tag{5}$$