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Non-isothermal pyrolysis characteristics of giant sensitive plants using thermogravimetric analysis

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ABSTRACT

A giant sensitive plant (*Mimosa pigra* L.) or Mimosa is a fast growing woody weed that poses a major environmental problem in agricultural and wet land areas. It may have potential to be used as a renewable energy source. In this work, thermal behaviour of dried Mimosa was investigated under inert atmosphere in a thermogravimetric analyzer at the heating rates of 10, 30, and 50 °C/min from room temperature to 1000 °C. Pyrolysis kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined. Two stages of major mass loss occurred during the thermal decomposition process, corresponding to degradation of cellulose and hemicellulose between 200–375 °C and decomposition of lignin around 375–700 °C. The weed mainly devolatilized around 200–400 °C, with total volatile yield of about 60%. The char in final residue was about 20%. Mass loss and mass loss rates were strongly affected by heating rate. It was found that an increase in heating rate resulted in a shift of thermograms to higher temperatures. As the heating rates increased, average devolatilization rates were observed to increase while the activation energy decreased.

1. Introduction

Future contribution of renewable energy is vital as energy becomes increasingly scarce and expensive. Use of diverse biomass resources is projected to contribute to a major fraction of future energy demands. Nonetheless, competition between biomass supply for fuel or for food applications has been intensified in the recent years. This concern has resulted in growing interests in alternative, non-edible biomass resources such as perennial rhizomatous grasses; miscanthus (*Miscanthus*), switchgrass (*Panicum virgatum*), reed canary grass (*Phalaris arundinacea*), giant reed (*Arundo donax*) and bamboo because of their high yield potential, appropriate biomass characteristics, low input demand and positive environmental impact (Lewandowski et al., 2003; Basso et al., 2005; Scurlock et al., 2000). In Thailand, non-plantation biomass resources have been assessed for their energy potential and found to be promising (Sujjakulnukit et al., 2005). Weeds such as giant sensitive plants are viewed to have potential as an useful bioenergy source. Giant sensitive plant is woody member of the genus Mimosa, in the family Fabaceae comprising about 400–450 species. It is a woody invasive shrub that originates from tropical America. Now, it can be found in tropical and subtropical areas over many countries especially Australia, Thailand, Vietnam, South American, and African countries. It forms dense, thorny impenetrable thickets, particularly in wet areas. It is one of the worst environmental weeds. Owing to its strong, dense and woody stems, some small fraction of Mimosa is utilised as firewood, bean-poles, and as temporary fences. So far, there have been relatively few literatures reporting on utilisation of Mimosa as feedstock for bioenergy (Presnell, 2004; Wongsiriamnuay et al., 2008).

Thermal conversion technology is an attractive route to produce fuel gases from natural resources. When the thermal process is carried out in a reactor, the raw material undergoes pyrolysis, gasification and combustion. They are complicated processes consisting of several main chemical reactions and large number of intermediate reactions. Many alternative paths are available to the reacting compounds, depending on the process conditions. Physico-chemical compositions of the fuel are also important and decisive factors for the characteristics of the thermal conversion. Thermogravimetric analysis (TGA) can be an useful tool to study the thermal behaviour of materials. The rate of mass loss as a function of temperature and time is measured and provides a means to estimate the kinetic parameters in the thermal decomposition reaction. These data are crucial for efficient modeling, design and operation of pyrolysis process and related thermochemical conversion systems. To determine the effect of temperature and heating rate on their pyrolysis characteristics, the samples are pyrolyzed under non-isothermal conditions in a thermogravimetric analyzer. Many TGA studies have been carried out for pyrolysis of various non-edible biomass sources (Jeguirim and Trouve, 2009; Park et al., 2009; Kumar et al., 2008; Maiti et al., 2007; Erlich et al., 2006; Collura et al.,

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2005; Cao et al., 2004; Meszaros et al., 2004; Fisher et al., 2003; Müller-Hagedorn et al., 2003; Gronli et al., 2002; Karaosmanoglu et al., 2001). To the authors' knowledge, there has not yet been a report on pyrolysis characteristics of giant sensitive plants. The objectives of this investigation are therefore to study pyrolysis characteristics and to analyze change of kinetic behaviour with conversion for the giant sensitive plant. Comparisons are made against other biomass sources.

2. Methods

2.1. Samples

The samples of Mimosa collected in agricultural zone in Chiang Mai, Thailand were used. The collected stalks were cleaned and air dried naturally in a dry store room at ambient condition. The dried samples were crushed and grounded in a high speed rotary mill, and sieved to provide a feed sample in the size range of about 0.5 mm. Preparation of samples prior to analyses was conducted in accordance with TAPPI T 257 and T 264 standards. Contents of the major biopolymer constituents of the weed, holocellulose, lignin and solvent extractive components were evaluated using TAPPI standard methods. The solubilities of extractives in ethanol and benzene mixture as well as quantity of soluble substances in sodium hydroxide and in water were established. ASTM standard methods were followed to carry out proximate analysis for the samples. The carbon, hydrogen and nitrogen contents were determined using a CHN elemental analyzer. The oxygen content was calculated by difference. The heating value of the dried Mimosa stalk was determined in compliance with ASTM standard using a Parr bomb calorimeter. It was reported as a gross heat of combustion at constant volume. Analysis results of the dried Mimosa samples are shown in Table 1.

2.2. Thermogravimetric apparatus

Thermal decomposition of the biomass materials were analyzed using a TGA/SDTA 851e thermogravimetric analyzer (sensitive microbalance, 1 μg resolution, 1300 °C maximum temperature at atmospheric pressure, 50 bar maximum at 1000 °C, and 30 °C/min maximum heating rate). This high performance TG analyzer has high sensitivity, vibration resistance and structure that permit rapid replacement of samples. Large number of samples can be analyzed in a short time and in succession. The system was logged to a personal computer for data handling and analysis. Prior to TGA, temperature, weight and sample platform calibrations were carried out. Each sample was placed in the platinum pan securely and in such a way that it was confined within the pan sides and not in contact with the sides of the oven. All handling of samples were done using brass tweezers to avoid contamination. Non-isothermal experiment runs were carried out at 10, 30, and 50 °C/min under atmospheric pressure, with an initial weight sample of 5 mg and a purge gas flow of 50 cm^3/min. The purge gases used were high purity nitrogen, air or oxygen. The sample was initially preheated to and equilibrated at 40 °C in nitrogen under a flow rate of 50 cm^3/min for 10 min. The sample was then heated to 1000 °C at a constant heating rate. The continuous records of weight loss and temperatures were obtained. At least three runs were performed for each condition.

Table 1
Analysis of dried Mimosa samples.

Property	Unit	Method	Quantity
Proximate analysis			
Moisture	(% w/w)	ASTM D 3173	1.6
Volatile	(% w/w)	ASTM D 3175	71.1
Fixed carbon	(% w/w)	ASTM D 3172	23.6
Ash	(% w/w)	ASTM D 3177	3.7
Ultimate analysis			
Carbon	(%)	ASTM D 3174	43.9
Hydrogen	(%)	ASTM D 3174	6.0
Nitrogen	(%)	ASTM D 3174	1.4
Oxygen	(%)	By difference	48.7
Lignocellulosic content			
Holocellulose	(% w/w)	Wise method	58.2
Lignin	(% w/w)	TAPPI T 222	33.9
Higher heating value	(MJ/kg)	ASTM 5865	17.5

3. Results and discussion

3.1. Thermal decomposition

The proximate chemical compositions of Mimosa stems were found to be similar to hard woods, but with higher ash content (Nordin, 1994). Ultimate analysis showed that raw Mimosa consisted of moderately high carbon content (43.9%) and low amounts of hydrogen (6.0%) and nitrogen (1.4%). Cellulose and hemicellulose were presented in terms of holocellulose, accounting for nearly 60% of total mass. Lignin content of Mimosa was found to be relatively high (33.9%). During pyrolysis of lignocellulosic materials, mass losses occurred due to dehydration at low temperatures, decomposition of hemicellulose, cellulose and lignin. Decompositions of these components were normally overlapped (Jeguirim and Trouve, 2009).

Thermal decomposition behaviours of Mimosa pyrolysis under flowing nitrogen were obtained. The results of thermogravimetric experiments were expressed as conversion α, defined as:

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \quad (1)$$

where W_i, W_t and W_f are the initial mass of the sample, the mass of pyrolyzed sample, and the final residual mass, respectively. The degree of conversion versus temperature at different heating rates of 10, 30 and 50 °C/min for the giant sensitive plant in TG analyzer are shown in Fig. 1. At the temperature lower than 150 °C, the small change of conversion in the samples was attributed to vaporisation of moisture that was attached on the surface of the samples. The giant sensitive plant samples started to decompose and release volatile matter around 200 °C. The TG curves of the giant sensitive trees showed only two major weight loss stages between 200 and 400 °C, and 400 and 700 °C. It was clear that the slope of the curve changed between the two temperature intervals. Slope between 200 and 400 °C was higher than that 400 and 700 °C. The conversions at different heating rates exhibited similar patterns. It was observed at temperatures below 400 °C that the TG curve shifted slightly to the right with increasing heating rate. At low heating rates, several distinct mass loss zones observed were associated with degradation dynamics of main constituents. Since the samples contained mainly cellulose, hemicellulose and lignin, it was known that the hemicellulose started to decompose at around 225–325 °C and the cellulose was found to decompose between 325 and 375 °C. Lignin had a broad decomposition temperature range at temperatures higher than 250–500 °C (Shafizadeh, 1985; Di Blasi and Lanzetta, 1997; Ferdous et al., 2002). As the heating rate was increased, these thermal degradation zones tended to merge. Simultaneous participation of all components cannot be avoided in measured mass loss (Di Blasi, 2008). Decomposition at 500 °C or higher progressed slowly due to the remaining lignin or char, similar to that reported by Fisher et al. (2003).