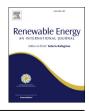
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## Evaluation of pyrolysis characteristics of milled bamboo using near-infrared spectroscopy

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#### ABSTRACT

This paper reports the development of a rapid and low-cost method based on near-infrared spectroscopy as an alternative for thermogravimetric determination of the pyrolysis characteristics, including Tonset, T<sub>sh</sub>, T<sub>peak</sub>, T<sub>offset</sub> and DTG<sub>peak</sub>, of milled bamboo. T<sub>onset</sub> is the extrapolated onset temperature that is calculated from the partial peak resulting from the decomposition of the hemicellulose component, T<sub>sh</sub> is the temperature corresponding to the overall maximum of the hemicellulose decomposition rate, DTG<sub>peak</sub> is the overall maximum of the cellulose decomposition rate, T<sub>peak</sub> is the temperature corresponding to the overall maximum of the cellulose decomposition rate and Toffset is the extrapolated offset temperature of the DTG<sub>peak</sub> curves determined using thermogravimetric analysis (TGA). The models may be used to control the pyrolysis processes of bamboo to achieve the most economical and environmental conditions. 80 samples of bamboo with various circumferences of culms in the ranges of approximately 16-18, 18-20, 20-22, 22-24, 24-26, 26-28, 28-30, 30-32, 32-34, 34-36, 36-38 and 38-40 cm were randomly collected for optimization of the models. The models were optimized by partial least squares regression (PLSR) with 80% of samples for the calibration set and 20% for the validation set. For Tonset, Tsh,  $T_{\text{peak}}$ ,  $T_{\text{offset}}$  and  $\text{DTG}_{\text{peak}}$ , the models showed coefficients of determination (R<sup>2</sup>) of 0.566, 0.845, 0.917, 0.973, and 0.671; root mean square errors of prediction (RMSEP) of 9.7 °C, 4.36 °C, 3.77 °C, 2.66 °C, and 0.428 wt loss %/min; ratios of prediction to deviation (RPD) of 1.52, 2.58, 3.48, 3.55, and 1.75; and biases of -0.344 °C, -0.765 °C, 0.349 °C, -5.41 °C, and 0.045 wt loss %/min, respectively. In addition, the results showed that pyrolysis characteristics did not depend on the circumference. The vibrational bands of water and CH<sub>3</sub>, O–H stretch, first overtones of Ar–OH, CH<sub>2</sub> and HC=CH in the cellulose and lignin structures, O-H hydrogen bonds of polyvinyl alcohol and C-H stretch corresponding to the first overtone of CH<sub>2</sub> had the highest influence on the values of Tonset, Tsh, Tpeak, and Toffset, respectively. The vibrational band of the C–O–C asymmetrical stretches of cellulose and hemicellulose, and the combination of O–H stretch and HOH bend of polysaccharides influenced the DTG<sub>peak</sub> value. These results are beneficial for studying the thermal behaviour of milled bamboo as a potential resource for producing biofuels, especially in the pyrolysis process.

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#### 1. Introduction

Biomass has drawn interest because it can act as a renewable and sustainable energy source. Owing to climate change and the increasing demand for fuel, biomass has become more interesting than ever [1]. Bamboo is a renewable energy crop that has been planted in many parts of the world. It is used for furniture,

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http://dx.doi.org/10.1016/j.renene.2016.10.080 0960-1481/© 2016 Elsevier Ltd. All rights reserved. apparatus and fuel. According to literature [2,3], bamboo has a short growth cycle and provides high yields of natural resources. Several studies have reported the advantages of bamboo, such as its fast growth [1,4], high energy and low ash [5], easy propagation and high productivity [6]. Bamboo is a large, woody grass [5]. In addition, some species can grow up to a foot a day [1]. It has been previously noted that bamboo could be the biomass material and bio-energy resource of the future [4,7].

The chemical components of biomass are important in the conversion process. Generally, biomass consists of three components, including hemicellulose, cellulose and lignin [8–11]. Some

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## ARTICLE IN PRESS

#### J. Posom et al. / Renewable Energy xxx (2016) 1-13

Table 1

Hemicellulose, cellulose and lignin content in bamboo.

Material	Hemicellulose	Cellulose	Lignin	Reference
Bamboo	15-20%	35-45%	15-25%	[50]
Bamboo	24.2	43.1	27	[5]
Bamboo Shoots (Bambusa blumeana)	$27.30 \pm 2.8$	$27.90 \pm 1.2$	$7.92 \pm 0.0$	[51]
2-Year-old (Bambusa blumeana)	27.51 ± 1.7	37.70 ± 1.5	$25.73 \pm 0.0$	
5-Year-old (Bambusa blumeana)	$22.94 \pm 2.1$	$41.91 \pm 1.0$	27.11 ± 0.3	
3-year-old moso bamboo culms (Phyllostachys pubescens)	$22.86 \pm 2.19$	$41.72 \pm 2.37$	$20.91 \pm 0.24$	[52]

studies have reported the content of hemicellulose, cellulose and lignin in bamboo (Table 1). This lignocellulosic matter shows different thermal behaviour during pyrolysis [12]. Pyrolysis is thermal decomposition that occurs in the complete absence of oxygen [13]. It is the technology used for converting biomass into energy and chemical products, which consist of liquid bio-oil, solid biochar and gas [14]. Many factors, i.e., temperature, particle size, heating rate and type of biomass affect both the rate and yield of pyrolysis [15]. The proportions of the chemical components of biomass affect the pyrolysis rates [16,17]. A higher lignin content (corresponding to lower cellulose) results in slower decomposition, while higher hemicellulose and cellulose contents lead to faster decomposition [16–19]. Stefanidis et al. [20] reported that pyrolysis of cellulose gave high yields of bio-oil; high content of hemicellulose gave high gas yields and moderate yields of bio-oil; and high content of lignin gave the highest solid residue yield. Hemicellulose and cellulose were quickly decomposed at 220–315  $^\circ\text{C}$  and 315-400 °C, respectively, while lignin was decomposed in a wide temperature range from 160 to 900 °C [11]. Hemicellulose decomposition had a shoulder peak at 290 °C, cellulose decomposition occurred at the highest peak at 347 °C, while lignin was decomposed in a wide temperature range without an observable peak [21]. Hisham et al. [22] found that the holocellulose, lignin and ash of the specie Gigantochloa scortechinii increased as the age was increased over 0.5, 1.5, 3.5, 5.5 and 6.5 years. Cheng et al. [23] showed that cellulose content decreased, and lignin and ash contents increased with the increase in bamboo age from one year to three years. Darabant et al. [2] showed vast differences in the bamboo yield as a result of site and plantation management in eastern Thailand. Thus, even the same species of bamboo may have different characteristics. On the other hand, harvesting age,

plantation management and soil fertility also influence the characteristics of bamboo, which have a definite effect on the thermal behaviour. Thus, rapid checking of pyrolysis characteristics of bamboo is required during pyrolysis because temperature influences the quality and yield of the biofuel. The pyrolysis characteristics, i.e., Tonset, Tsh, Tpeak, Toffset, and DTGpeak, are illustrated in Fig. 1. El-Sayed and Mostafa [12] indicated that Tonset was the extrapolated onset temperature calculated from the partial peak that results from the decomposition of the hemicellulose component, T<sub>sh</sub> was the temperature corresponding to the overall maximum of the hemicellulose decomposition rate, DTG<sub>peak</sub> was the overall maximum of the cellulose decomposition rate (dm/dt at the highest peak, wt loss %/min), T<sub>peak</sub> was the temperature corresponding to the overall maximum of the cellulose decomposition rate and Toffset was the extrapolated offset temperature of the DTG<sub>peak</sub> curves determined using thermogravimetric analysis (TGA). Thermogravimetric (TG) analysis is the direct measurement of weight changes on the TG chart of each sample, and this technique requires a highly skilled technician. These properties can be used to control thermal and chemical conversion during the pyrolysis of biomass.

Bamboo, like wood, consists of hemicellulose, cellulose and lignin, which are formed by the atoms C, O and H [24]. Nearinfrared (NIR) radiation interacts with structure of O–H, N–H, C–H, C–O, C–O–C, HC=CH, C=C and so on [25,26]. Hence, biomass is a good absorber of NIR radiation. NIR spectroscopy is an appropriate and rapid method for evaluating the components and physical properties of agricultural products. Rapid methods are needed to characterize biomass for energy because of the increasing use of biomass in energy systems and the expanding varieties of biomasses available [13]. The different characteristics of

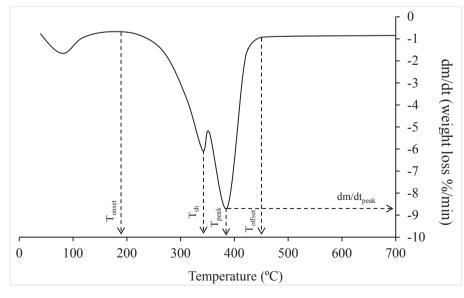


Fig. 1. TG profile for characteristic properties of the material, based on thermal degradation.

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