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Investigation of Characteristics and Thermal Behaviour of Lignocellulosic Waste Biomass Using Thermogravimetric Analysis

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Abstract
This paper focuses on lignocellulosic waste biomass originating from food industry, which should find its further application in order to fulfill demands of circular economy. Therefore, here are presented some of the chemical and physical properties that affect combustion process, as well as thermochemical reaction kinetics for lignocellulosic biomass wastes. The biomass investigated was peach stone particles originating from food industry. The results have showed that peach stones can be characterized as good energy alternative renewable material, with properties that allow its safe thermochemical conversion. Kinetic analysis of this biomass was performed using Thermogravimetric Analysis (TGA) with a simple reaction model applied, namely n-th order reaction model. The obtained results have confirmed the complex nature of this material and the need for further modelling.

1. INTRODUCTION

The decrease in traditional fossil fuel reserves has increased the interest in findings of alternative fuels from various biomasses. Biomass fuels represent a variety of materials such as wood, energy crops, energy plantations, agricultural and agro-industrial byproducts and wastes (Arvelakis et al., 2005). These materials can be used as the sole fuel or in combination with fossil fuels for energy production via thermochemical conversion methods. Especially interesting is waste biomass, which represents a renewable energy source, but with some constraints and limitations regarding its composition and thermochemical conversion process. Lignocellulosic waste biomass is mainly comprised of cellulose, hemicellulose, and lignin, with small amounts of extractives, moisture, and mineral matter (Órfão et al., 1999). The combustion of biomass may be associated with certain risks such as fire-explosion risk, excessive slagging and ash formation, as well as chlorine corrosion, so the knowledge of the physicochemical properties of biomass allows proper selection of the biomass type, as well as the amount of combusted biomass to ensure its minimal impact on the firing system (Lalak et al., 2016). At the same time, this will give certain directions in biomass pretreatment, which will help in minimizing the negative impact both on combustion system and the environment. Pyrolysis is one of the fundamental thermochemical conversion processes that can be used to transform biomass into fuels. Therefore, the understanding of pyrolysis kinetics is very important in biomass conversion application (White et al., 2011). One of the most commonly applied thermo analytical techniques in solid-phase thermal degradation studies is thermogravimetric analysis (TGA). TGA can be used to investigate the thermal behavior of any material, by providing the information about thermal stability and the process of material degradation with the change of temperature (Lopičić et al., 2017). According to many authors, prior knowledge of reaction kinetics is crucial before any attempt to utilize biomass as a feedstock for thermochemical processes (Sait et al. 2012). In this paper, the authors have investigated some of the properties of biomass which play an important role in biomass application as energy source. Also, the thermochemical process that occurs in the treated material is discussed.

2. MATERIAL AND METHODS

The peach stone biomass was obtained from a local factory that processes fruits in order to obtain fruit based food and alcoholic/nonalcoholic beverages. The stones were washed with water and dried at room conditions. After drying, the stones were ground into powder by the ultra-centrifugal mill "Retsch ZM-1" (Retsch, Gemini BV, Netherland), and screened through a series of wire sieves. For the purpose of the experiments described in this paper, particles with diameter less than 0.1 mm were used. The complete procedure of sample preparation was described by Lopičić et al. (2016).

Thermal analysis of the samples was performed on a Netzsch STA 409 EP analyser, heating the sample in the nitrogen and air atmosphere at the temperature range from 25 to 900 ºC and at the heating rate of 10 ºC/min. Before the analyses, the samples were kept in a desiccator at the relative humidity of 23%. In each test about 10 mg of sample was used. During the process of thermal degradation, the initial weight was recorded continuously as a function of temperature and time.

The average bulk density of the PS samples was calculated from three samples, and tested as mass per unit volume method as described by Obernberger and Thek (2004).

3. RESULTS AND DISCUSSION

3.1. Biomass characterization

The lignocellulosic components present in the peach stone are reported to be: cellulose (62.94%), lignin (17.93%) and hemicellulose (5.42%) (Lopičić et al., 2013). Dry basis elemental compositions have showed that PS contains of 47.42% of carbon (C), 6.06% of hydrogen (H), 45.58% of oxygen (O), 0.27% nitrogen (N) and 0.21% sulphur (S), while the ash content was 0.46%. These data were used for calculating the heating value of peach stones (MJ/kg) using a correlation given by Channiwala and Parikh (2002). This correlation is proposed by the following equation:

$$CV(MJ/kg) = 0.3491 \cdot C + 1.178 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.0151 \cdot N - 0.0211 \cdot Ash \quad (1)$$

Table 1 contains some of the properties important for biomass characterization in the terms of fuels: the bulk density, caloric value and the ash content. These properties are compared with other biomasses found in literature. Bulk density is important in terms of storage and transportation of the feedstock and also determines the dimensions of the biomass handling system and the sample behavior during thermochemical processing (Sait et al., 2012). Low values of this parameter are not advised, since they not only reflect negatively on energy density, transportation costs and storage capacity (Obernberger and Thek, 2004), but also have a significant influence on biomass burning rate (Ryu et al., 2006). Obernberger and Thek (2004) investigated some of the physical characteristics and chemical composition of densified biomass fuels in order to analyze their combustion behavior, and noted that 650 m3/kg is often the desired value of wood pellet producers, in order to achieve appropriate energy and economic values. As can be seen from Table 1, groud PS particles have bulk density of 675 m3/kg, which is much higher compared to other biomasses, leading to the conclusion that PS can be directly used as a high energy content biomass fuel. The caloric value of PS calculated by Eq. 1 is 18.97 MJ/kg. This value is lower than the caloric value of hard coal for example, but higher than most of the caloric values found in literature (Lalak et al., 2016), and also high enough to empower the utilization of this biomass type as energy source. The ash content in biomass fuels can vary depending on many factors, ranging from 1% wt. basis in the case of wood to up to 15-20% in the case of some agricultural residues (Lalak et al., 2016). However, the ash content of the peach stone biomass was very low, 0.46%, indicating good combustion behavior, and high burning rate. Low ash content also has a positive effect on minimizing agglomeration, operational and disposal costs, avoiding slagging and fouling on the combustion unit's components. maximum weight loss in the range of 220°C to 380°C, which corresponds to overlapping reaction mechanisms between hemicellulose, cellulose and lignin. In pyrolysis, the maximum weight loss occurs at the temperature range from 210 to 410°C, with the strong peak at 316.8°C.).

Table 1. Biomass properties important for fuel characterization

Biomass type	Bulk density, m^3/kg	Caloric value, MJ/kg	Ash, %	Reference
Palm leaf	298	17.90	11.7	Sait et al. (2012)
Pine	285	18.30	1.20	Ryu et al. (2006)
Miscanthus	660	15.40	12.9	Ryu et al. (2006)
Wood pellets	591	20.30	0.51	Obernberger, I. & Thek, G. (2004)
Cotton stalk	310	17.4	5.10	Munir et al. (2009)
Peach stones	675	18.97	0.46	This paper

The elemental analysis of the PS sample showed a low level of sulfur and nitrogen, indicating that this material would produce low emission of acid gases, such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x). At the same time, the absence of chorine has a positive effect on corrosion behavior of this waste.

3.2. Characteristics and kinetic parameters of PS pyrolysis samples characterization

Typical TG and DTG analysis of lignocellulosic PS biomass pyrolysis was done in a nitrogen environment. The samples were subjected to constant heating rate of 10°C/min. The obtained data are given in Figure 1. The generated derivative (DTG) curve showed the weight loss of sample per unit time against temperature. The initial loss in weight of the samples occurred at the temperature range from 30°C to 115°C and was due to the evaporation of water content, which was about 4.5 wt. % for the PS sample. Another peak observed at up to 210°C may correspond to easily volatile compounds. The burning environment (nitrogen/air) as well as the chemical composition of the biomass strongly influences some of the parameters of thermochemical conversion, such as the initial ignition temperature, peak temperature and burning rate (Sait et al, 2012). The thermal analysis of the PS sample performed in an oxygen atmosphere showed the typical three-stage mechanism, with

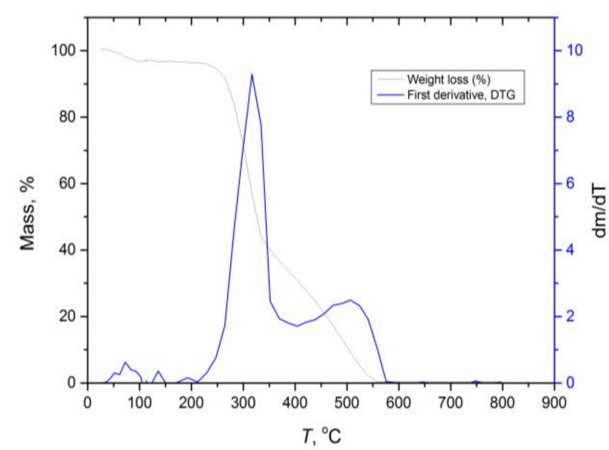

Figure 1. TG/DTG curve of PS pyrolysis (heating rate 10 °C/min)

These overlapping mechanisms increase the complexity of the PS degradation reactions chemistry (Lopičić et al. 2017) This temperature range is in agreement with literature data for materials with similar chemical composition (Sait et.al, 2012, Chen et al, 2015). The data obtained by thermogravimetric analyses were used to investigate the kinetics of the reaction that results from thermal degradation. The reaction kinetics of any combustion process can be expressed by the following decomposition rate equation, where the dependence of the process rate on temperature, k (T), is expressed by the Arrhenius equation:

$$k = A\exp(-\frac{E_a}{RT}) \quad (2)$$

$$\frac{d\,\alpha}{d\,t} = k(T) \cdot f(\alpha) \quad (3)$$

$$\alpha = \frac{m_o - m_t}{m_o - m_\infty} \quad (4)$$

where k(T) represents the rate constant, $f(\alpha)$ is a general expression of the reaction mechanism and α represents the extent of conversion at time t, masses m_o, m_t, and m_∞ refer to the initial, instantaneous, and final mass of the sample, respectively; Ea and A are the activation energy (kJ/mol) and the pre-exponential factor (1/min), R is 8.314 J/Kmol, and T is absolute temperature (K). The kinetics of a non-isothermal combustion process, under the heating rate β, that assumes the reaction of n-th order, n, is described as:

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(-\frac{E_a}{RT}\right) \cdot (1-\alpha)^n \quad (5)$$

For n=1, $g(\alpha)$ = -ln(1-α) giving:

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

Equations 6 and 7 should result in a straight line with slope $-E_a/R$ and an intercept of ln $[AR/\beta E_a]$. Thus, by plotting the left-hand side of Eqs (6 and 7), vs. $1/T$, the kinetic parameters E_a and A from the slope and intercept were calculated. The values of α and T obtained from the TG analysis were used and appropriate graphs presented in Figure 2 were drawn. For the purpose of this paper, the graphs for the first order (n=1) and fourth order (n=4) are presented. The criterion used for the acceptable values of E_a and A was the bigger final value of the linear correlation coefficient. The calculated values of E_a were 31.44 kJ/mol for n=1, and 98.44 kJ/mol, for n=4. As seen from Figure 2, increasing the order of reaction increased the value of the correlation coefficient, indicating that the thermal degradation of a lignocellulosic structure such as PSs is more complex with several stages which should be considered separately, as indicated by several authors (Chen et al, 2015, Vyazovkin et Wight, 1999). Compared with literature data for the materials of the similar chemical composition, the value of activation energy obtained for the fourth order reaction appears to be more realistic. At the same time, this value is much lower than the ones described by Chen et al. (2015), who stated that this kind of biomass should be investigated by applying more complex three-parallel-DAEM model which incorporates three parallel reactions. The authors have stated that the mean activation energies for hemicelluloses, cellulose and lignin were in the range of 148.12–164.56 kJ/mol, 171.04–179.54 kJ/mol and 175.71–201.60 kJ/mol, for the materials with the mass fractions of hemicelluloses, cellulose and lignin estimated to be 0.12–0.22, 0.54–0.65 and 0.17–0.29, respectively.

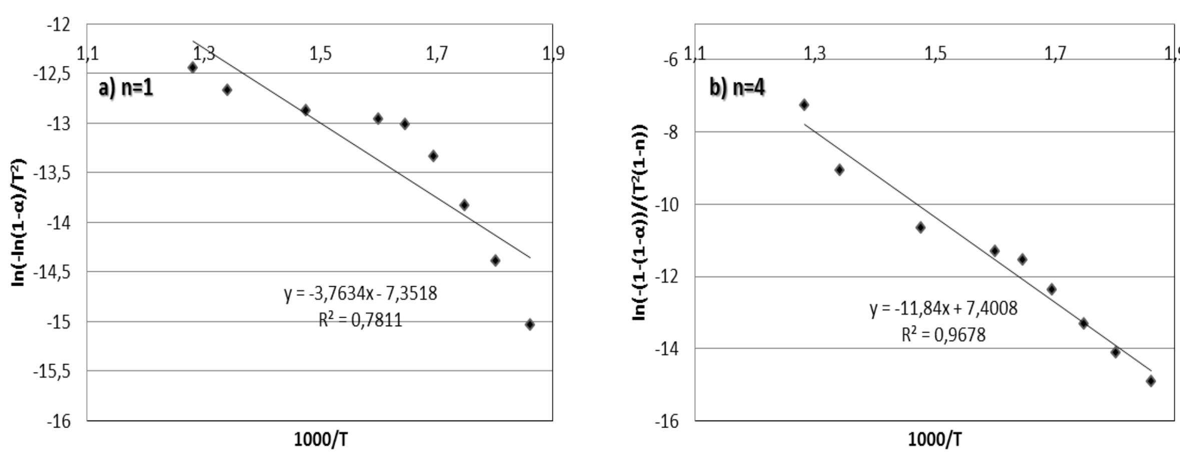

Figure 2. Kinetic plots for PS pyrolysis modelled by n-th order reaction model (10 ºC/min)

For n≠1, $g(\alpha)$ = (1-(1-α)$^{(1-n)}$) / (1-n), resulting in:

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

4. CONCLUSONS

Lignocellulosic waste materials have certain energetic properties which have to be used in order to fulfil sustainability demands of the future. Peach stone particles described in this paper, have certain physical and chemical properties which satisfy the request for energy density, small ash content and safe burn out. Further investigation should include the composition of the ash and its main constituents affecting fouling and corrosion behavior. The kinetic data obtained from thermogravimetric analysis were based on the Arrhenius equation, which is used by many researchers. It is concluded that the thermal degradation of PS is the complex processes due to its chemical composition, so no single kinetic model can be used. Further investigations including other more complex multistep models are needed.

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