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Thermodynamic Parameters of a Solid Biofuel from Orange Peel

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The global energy scenario is a widely discussed topic in these days, with growing concern about the future supplies. Thus, much attention has been given to the utilization of biomass as an energy resource. In this way, the orange peel becomes a material of great interest, especially to Brazil, which has around 9.5 million tons of this waste per year. The current research focuses and aims potential use of dried orange peels as solid biofuel. Thermal analysis of the dried peel showed three events of mass loss, and that the thermal stability of the material increases with an increase the pyrolysis temperature. The activation energy was calculated by using Osawa-Flynn-Wall method for the global process observed during the heating from the 25°C up to 600°C. The tests carried out indicated the potential use of waste orange peel as a solid biofuel material.

1. Introduction

The use of biomass as an energy resource has acquired great visibility as an alternative route to the consumption of fossil fuels (Kim et al., 2010; Protasio, 2013), highlighting the use of fruit peel or parts of plants, mainly because they are reused, since they are waste of agricultural activity (Vieira, 2011). These residues, apparently without viable application, may result in various environmental adversities due to improper disposal (Giusti, 2009; Brown et al., 2011; Guerrero et. al., 2013; Marshall and Farahbakhsh, 2013).

The use of biomass can be one way to reduce the pressure on natural resources directly exploited for the production of fuels (Filippetto, 2008; Schütz et al., 2010; Miura et al., 2011). It is estimated that currently about 15% of primary energy consumption worldwide comes from the use of this feature. In some developing countries this percentage may increase to 28% to 65%.There are many processes that could be applied to these discharges with an objective of changing them into products with a higher benefit, such as biofuels (Shuping et al., 2010). One of the most process conversion processes utilized is pyrolysis, a thermal decomposition of organic substances, at lower oxygen levels, in different phases (Maschio et al.,1992; Bridgwater and Peacocke, 2000; Bridgwater, 2003; Huang et al., 2011).

Today Brazil is the largest producer of orange juice in the world, therefore the largest generator of waste orange, coming in nearly its entire manufacturing process of juice. Are processed annually around 10 Mt of oranges, representing more than 49 % of the Brazilian production of fruits, and 53 % of world production of orange juice, 80 % of this production is in the state of Sao Paulo (IBGE, 2014). Orange has major waste shells, membranes and citrus waste, which are high in soluble carbohydrates and polysaccharides, with high potential for biological conversion. Solid waste as bark, seeds and pulp, representing 50% of the fruit weight, containing 82% moisture, while the liquid residue (yellow water) has a high content of organic matter with a high polluter factor (Tavares et al., 1998). The composition of the waste, in particular the orange peel, owns 16.9% of soluble sugars, 9.21 % cellulose, 10.5 % hemicellulose and 42.5 % pectin. Lignocellulosic biomass is characterized as a complex mixture of carbohydrates of natural polymers, known as cellulose (crystalline polymer of glucose), hemicellulose (complex polymer, amorphous, being its major component a monomer unit of xylose) and lignin (not polyaromatic compound condensate large chain) and small fractions of other substances, such as statements (Huber at al., 2006).With this arrangement the bark has a high potential for production of compounds from chemical or enzymatic (ABECITRUS, 2014) hydrolysis. However, it still has the problem of proper disposal of this waste, caused mainly by the large amount generated in the production

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process of orange juice. Recently studies have shown the greatest increase in environmental contamination due to the quantity and inadequate waste disposal, which have caused serious environmental problems in organisms and humans. The industrial-scale processes produce waste with a high concentration of toxic elements, and conventional treatments for the removal or reduction of these impurities, such as heavy metals have high costs and restrictions, since they can not ensure the reduction of toxic components to the minimum extent permitted by regulatory standards established by environmental agencies (Bayramoglu, 2008). One of the major causes are the effluents of industries that produce different constitution each other, with various types of organic and inorganic pollutants (Figueiredo et al., 2005), (Sorja et al., 2005), (Namasivayam and Sumithra, 2005), (Abdelwahab et al., 2006), (El-Sikaily et al., 2006), (Noroozi et al., 2007). The use of biomass for the production of new chemical compounds with energy use is directly linked to sustainable development and marketability of its products, being a major conversion processes is pyrolysis Bridgwater (1999). Due to its composition is rich in soluble and insoluble carbohydrates, this product has great potential to be used in high value-added products obtained by different processes of biomass conversion. Thus, the use of this waste to supplement the energy capacity of the country can be considered as a viable alternative and sustainable, he biomass converted into biochar process using high efficiency pyrolysis, produce high quality coals, or high calorific value, fixed carbon content above 90% and ash content below 0.5%. A biochar with these characteristics has a high energy yield, as well as an excellent economic profitability and is important to the economy of many countries. One of the advantages of using this product would be to reduce the use of fossil fuels, are used today on a large scale worldwide. (Neves, 2010; IBGE, 2010). One of the main advantages of using biomass is the direct use, the combustion in furnaces, boilers, among others. This procedure is characterized by a very rapid exothermic reaction between the fuel and the oxidant, followed by heat release, however, has low efficiency (Carvalho e Mcquay, 2007). The knowledge of the kinetic parameters involved in the reactions of thermal conversion is fundamental to the design and optimization of biomass pyrolysis reactors. Thus, the process of decomposition of biomass has attracted increasing attention (Shuping et al., 2010; Damartzis et al., 2011). In addition to optimizing the thermodynamic parameters are useful for understanding and calorific behavior of the studied biomass, these results can provide us with important information about the reactions that take place throughout the process of pyrolysis and / or burning of this product. It is also important for calculation of efficiency and application on an industrial scale, and to think of a sustainable energy system. For each kind of application should be respected the particularities of the process. The material used must have certain characteristics. In this work the authors studied the kinetics of the thermal processing of dried orange peel, with the purpose of generate data for a discussion of the potential applicability of this material as an alternative energy source.

2. Methodology

2.1. Raw material

The orange peels were taken from the Institution Educandário Bezerra de Menezes (Sorocaba, Sao Paulo), Pear variety (*Citrus sinensis*). The peels were washed with distilled water and detergent, reduced to fragments of approximately 5x5 cm then placed in a stove (Solab 100/42) at 110 °C for three days to complete drying of the sample. After drying, the peels were crushed and sieved through #200 mesh sieves. A number of analytical steps were performed on a single batch in order to minimize potential differences, since the chosen variety is present in all the Brazilian territory.

2.2. Thermal analysis

For thermogravimetric analysis (TG) and its derivative (DTG) the analyzer TGA-DTA-DSC, simultaneous TA Instruments (SDT-Q600) were used. Approximately 2 mg of the samples were placed in alumina crucibles, using nitrogen as carrier gas at flow rate of 100 $mL.min^{-1}$. The samples were heated from 20 °C to 600 °C, at heating rate of 10, 15 and 20 $°C.min^{-1}$.

2.3. Thermodynamics parameters

The thermodynamic parameters, enthalpy (ΔH°), Gibbs free energy (ΔG°), entropy (ΔS°) and the pre-exponential factor (A), were determinate by Ozawa-Flynn-Wall method for the global process observed during the heating of the material from the 25 °C up to 600 °C, according to the equations:

$$\ln(\beta) = C\alpha - Ea/(RT) \qquad (1)$$

Where E_a, β, C (α), R and T are respectively the activation energy, heating hate, mechanism function, universal gas constant and temperature.

$$A=\beta.E_a.\exp(\frac{E_a}{R\,T_m})/(R.T_m^2) \tag{2}$$

$$\Delta H^{\circ}=E_a-RT \tag{3}$$

$$\Delta G^{\circ}=E_a+R.T_m.\ln(\frac{K_b.T_m}{H.A}) \tag{4}$$

$$\Delta S^{\circ}=\frac{\Delta H^{\circ}-\Delta G^{\circ}}{T_m} \tag{5}$$

Were K_b, h and T_m are the Boltzmann constant, Plank constant and DTG temperature peak.

3. Results and discuss

3.1 Thermal analysis

The mass loss curve (TG) and its derivative (DTG) of the dried powder of orange peel (inert atmosphere, until temperature of 600 °C at heating rate of 10 °C min^{-1} are shown in Figure 1.

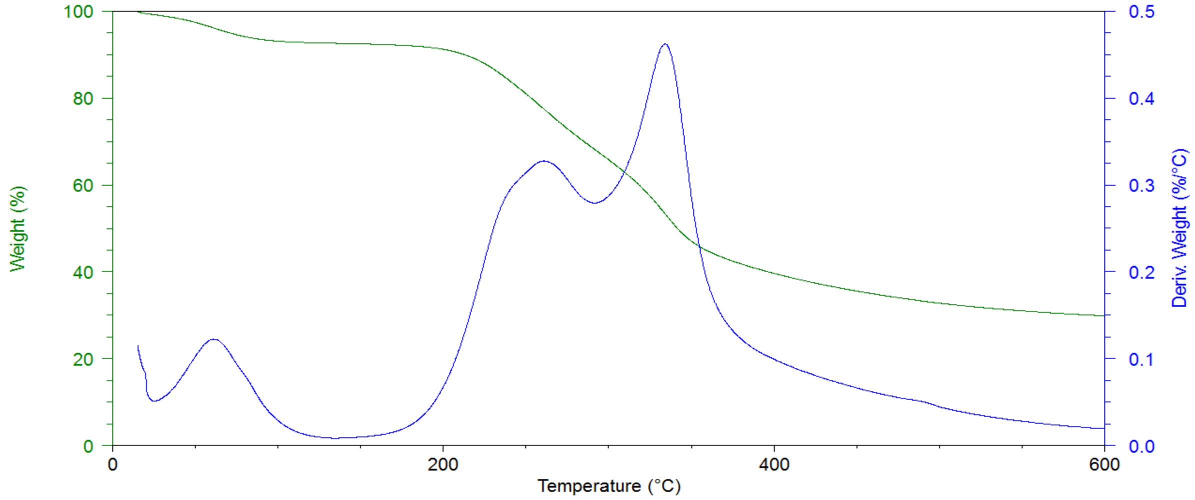

Figure 1. Mass loss curve (TG) and its derivative (DTG) of dried orange peel (Adapted from Santos and Morais, 2014b; Santos and Morais, 2015).

Through TG analysis can be observed three events of mass loss. Until a temperature of 150 °C is related to loss of water in the sample; 150 °C to 350 °C has a loss of mass due to the decomposition of organic components, compatible to that described by Orfão and Figueiredo, they demonstrated that at temperatures below 230 °C prevailing degradation of hemicellulose; in the range between 230 and 260 °C it is observed the decomposition of hemicellulose and cellulose; and between 260 and 290 °C, there is the end of the decomposition of hemicellulose, predominantly below the decomposition of the cellulose; the third stage of mass loss from 350 °C onwards is related to lignin degradation. At the end, found 20 % residual mass.

3.2 Thermodynamics parameters

The activation energy was determined from the Ozawa-Flynn-Wall method. TG curves of biomass in an inert atmosphere at different heating rates is shown in Figure 2. The kinetic parameters of weight loss as the activation energy (Ea) and pre-exponential factor (A) are shown in Table 1.

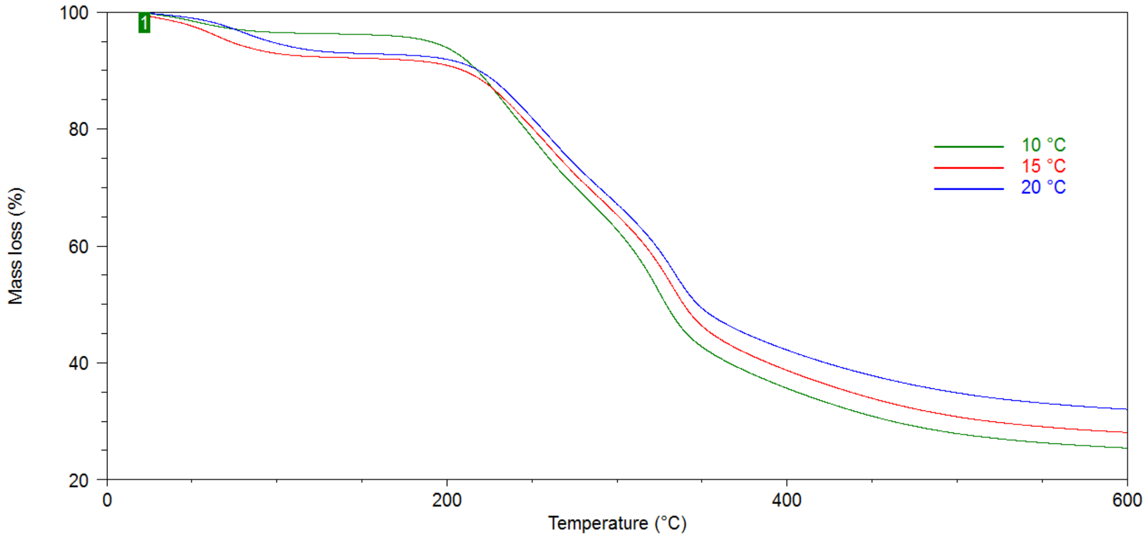

Figure 2. Thermogravimetric curves of dried orange peel dried at heating rates of 10 ° C, 15 ° C and 20 ° C per minute in an inert atmosphere (Adapted from Santos and Morais, 2015).

Table 1. Thermodynamic parameters of the dried orange peel under inert atmosphere (Adapted from Santos and Morais, 2014[a]; Santos and Morais, 2015)

Ae (kJ/mol)	A (s^{-1})	ΔH° (kJ/mol)	ΔG° (kJ/mol)	ΔS° (J/mol)
92,6	1,44E+7	87,6	161,6	-121,7

The activation energy in this work was determined based on the method of Ozawa-Flynn-Wall (KIM et al., 2010).

The thermodynamic parameters ΔH°, ΔG° and ΔS° were calculated for the temperature T = Tp, where Tp is the peak of DTG, this is characterized as the highest temperature of the process (KIM et al., 2010).

For each type of application, the material used must possess certain characteristics, for example, the material to be used for syngas should not break easily, its apparent density should not exceed 0.3 g / cm^3 and must submit a 75% carbon content; already for the chemical industry requirements vary according to the use of the material, however, in general, require good purity is tied to a good chemical reactivity . Thus, the dried orange peel have potential use as an energy resource because there was a high percentage of residual carbon and in addition, has no toxic elements because its composition is organic (GOLDEMBERG et al., 2000).

4. Conclusions

According to the experimental results, TG / DTG curves done in nitrogen atmosphere of the dry orange peel showed three phases of mass loss with residual mass of 20 %.

The thermodynamic parameters determined characterize a material of high reactivity, where the system can react faster to produce an activated complex, and consequently, shorter reaction times.

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