Kinetic parameters of red pepper waste as biomass to solid biofuel

Amanda Alves Domingos Maia, Leandro Cardoso de Morais *

Institute of Science and Technology, São Paulo State University (UNESP) "Júlio de Mesquita Filho", Av. Três de Março, 511, Alto da Boa Vista, 18087-180 Sorocaba, São Paulo, Brazil

HIGHLIGHTS

- Thermochemical conversion of biomass residues.
- Bioenergy.
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ABSTRACT

This work aimed to study the kinetic of thermal degradation of red pepper waste as solid biofuel to bioenergy production. The thermal degradation experiments were conducted at three heating rates, 5 °C/min, 7.5 °C/min and 10 °C/min in a thermogravimetric analyzer and oxidative atmosphere. The kinetic analysis was carried out applying the isoconversional model of Ozawa–Flynn–Wall. The activation energy was considerate low and varied 29.49–147.25 kJ/mol. The enthalpies revealed the energy difference between the reagent and the activated complex agreed with activation energies, the values of the pre-exponential factor indicated empirical first order reactions, Gibbs free energy varied from 71.77 kJ/mol to 207.03 kJ/mol and the changes of entropies had negative values, indicating that the degree of disorder of products formed through bond dissociations was lower than initial reactants. The calorific value was 19.5 MJ/kg, considered a relevant result for bioenergy production.

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1. Introduction

The agro-industry generates a large quantity the residues, also called biomass, which may be employed in the bioenergy generation. Several wastes are being used as biomass, including seeds, sewage sludge, leaves and algae (Santos et al., 2015b).

Worldwide data shows 1.3 billion of tons of food are wasted yearly which is equivalent to 750 billion dollars a year of damage (Food and Agriculture Organization, 2015).

Health-promoting, nutritional and sensory attributes make pepper as one of the most worldwide consumed vegetable (García, 2011) and *Capsicum sp.* powder is one of the most important spices. However, studies of the reuse and thermochemical properties of these residues have not been investigated (Santos et al., 2015b).

The red peppers cultivation has a greater importance and is considered the second most exported vegetable, encompassing an annual worldwide production of 30 million tons in an acreage of 4 million ha (Freibauer et al., 2011).

The production of this fruit is considered one of the most important, representing the third in production and vegetable consumption, second only to garlic and onion (Milagres, 2014).

The quality and quantity of the obtained bioenergy depend not only on the chemical composition of original biomass but also on the reaction conditions. Thus, it is important to understand the chemistry of this alternative biomass in order to know the thermochemically conversion process into biomass-derived fuels (Lee et al., 2014).

This paper examines thermochemical red pepper waste conversion including thermodynamic parameters for non-isothermal analyses using Ozawa–Flynn–Wall (OFW) kinetic isoconversional model. Then the values of apparent activation energy (E_α), pre-exponential factor (A) in Arrhenius equation, as well as the changes of entropy (ΔS), enthalpy (ΔH) and free Gibbs energy (ΔG) were calculated. The calorific value was determined by calorimetric bomb.

* Corresponding author. Tel.: +55 (15) 3238 3400x3429; fax: +55 (15) 3228 2842.
  E-mail address: leandro@sorocaba.unesp.br (L.C. de Morais).

2. Methods

2.1. Sample preparation

The biomass of this study was the red pepper, *Capsicum baccatum* var. *pendulum*, waste. At the laboratory, the biomass was washed in tap water and dried naturally at room temperature for 24 h, followed by oven drying Solab model SL-100/42 at 105 °C to constant weight. The whole process lasted about seven days. After drying, the samples were ground in a Wiley mill, MA048 – Marconi, followed by sieving, Solotest sieve, NBR #200 (0.074 mm).

2.2. Thermal analysis

Thermogravimetric analysis were carried out at three different heating rates, 5°, 7.5° and 10 °C min^{-1}, using a simultaneous DSC-TGA equipment, TA Instruments, model SDT Q600, from 25 °C to 1000 °C. Air was used as purge gas at a 120 ml min^{-1} flow rate. About (1.5 mg) of the biomass were used in alumina pans in each analysis. The TA Instruments software provides the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves.

2.2.1. Calorific value

It was used a Calorimetric Bomb IKA C-200 and about 0.5 g was used for 10 min with 99.5% pure oxygen.

2.3. Kinetic study

As a matter of fact, the isoconversional analysis provides a fortunate compromise between the oversimplified but widely used single-step Arrhenius kinetic treatments and the prevalent occurrence of processes whose kinetics are multi-step (Vyazovkin and Sbirrazzuoli, 2006).

The one-step global model assumes that the degradation processes results in a single reaction, below.

$$Biomass \xrightarrow{k} Volatiles + Biochar$$

k is defined as the rate constant of reaction whose temperature dependence is expressed by the Arrhenius equation

$$k = Ae^{(-E_a/RT)} \tag{1}$$

where:

E_a apparent activation energy (kJ/mol);
T is the absolute temperature (K);
R universal gas constant 8.31 J/K mol^{-1};
A is the pre- exponential factor (s^{-1}).

The rate of transformation from solid-state to volatile product is described by the following expression:

$$\frac{d_\alpha}{d_t} = k(T)f(\alpha) \tag{2}$$

where:

A is conversion degree of the process;
k (T) is the time of process;
f (α) is the rate constant and the reaction model.

Conversion, α, represent the normalized form of weight loss data of decomposed sample and is defined as below:

$$\alpha = \frac{m_i - m_\alpha}{m_i - m_f} \tag{3}$$

where:

m_i is the initial mass of the sample;
m_α is the actual mass;
m_f is the mass after combustion.

Combining Eqs. (1) and (2) gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of TG results.

$$\frac{d_\alpha}{d_t} = A * f(\alpha) * e^{-E_a/RT} \tag{4}$$

The expression of the function $f(\alpha)$ and its derivative f (a) are used for describing solid-state first order reaction:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where:

n is the order reaction.

Substituting expression (5) into Eq. (4) gives the expression of reaction rate in the form:

$$\frac{d_\alpha}{d_t} = A * (1 - \alpha)^n * e^{E_a/RT} \tag{6}$$

For non-isothermal TG/DTG experiments at linear heating rate $\beta = dT/dt$, Eq. (6) can be written as:

$$\frac{d_\alpha}{d_t} = \frac{A}{\beta} * (1 - \alpha)^n * e^{-E_a/RT} \tag{7}$$

This equation expresses the fraction of material consumed in the time. In this work the activation energy was obtained from non-isothermal TG/DTG. The methods used to calculate kinetic parameters were non-isothermal and isoconversional Ozawa–Flynn–Wall methods and required tests at different heating rates.

2.3.1. Ozawa–Flynn–Wall methods

Kinetic analysis is essential to design and establish efficient, safe and reasonable processes. Determination of thermo-kinetic behavior of biomass allows control of decomposition mechanism of biomass. Kinetic parameters of reaction are necessary for accurately prediction of reactions behavior and optimization of the process towards products during thermal degradation (Ceylan and Topçu, 2014). Non-isothermal thermogravimetric analysis is the most popular and simplest method to study the kinetics and thermodynamics properties of biomass. An isoconversional integral method seems to be a safer alternative for the calculation of meaningful activation energy values for certain prerequisites, without knowing the kinetic model of the reaction mechanism.

The Ozawa–Flynn–Wall kinetics isoconversional method Eq. (8) was applied (Kim et al., 2010).

$$ln(\beta) = C_\alpha - \frac{E_\alpha}{R \cdot T} \tag{8}$$

where:

β heating rate;
E_α apparent activation energy;
C_α function of the conversion degree α;
R universal gas constant 8.31 J/K mol^{-1};
T the absolute temperature (K).

It was applied at least three values of heating rate (β) for different and same values of α in different absolute temperatures (T) in Kelvin (K) obtained at thermogravimetric curves. Allows to investigate whether the mechanism of the conversion is changing with the conversion degree, estimating the respective activation energy E_α at a conversion degree α. To calculate the kinetic parameters this work used an intermediate value of β (7.5 °C/min).

The thermodynamic parameters using OFW isoconversional method for analysis of kinetic studies and thermodynamic parameters including pre-exponential factor (A) in Arrhenius equation, as well as enthalpy (ΔH), free Gibbs energy (ΔG) and the changes of