Bioresource Technology 219 (2016) 392–402

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Combustion reaction kinetics of guarana seed residue applying isoconversional methods and consecutive reaction scheme

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HIGHLIGHTS

- First study of oxidative thermal decomposition kinetics of guarana seed residue.
- Decomposition stages described by dehydration, oxidative pyrolysis, and combustion.
- First-order and two-dimensional diffusion mechanisms represented the main stages.
- Consecutive reactions scheme validated kinetic parameters from model-free method.
- Experimental and theoretical conversion and conversion rates were in good agreement.

ARTICLE INFO

Article history:
Received 29 May 2016
Received in revised form 22 July 2016
Accepted 23 July 2016
Available online 26 July 2016

Keywords:
Activation energy
Biomass
Combustion
Kinetics
Thermogravimetry

ABSTRACT

This work aims the study of decomposition kinetics of guarana seed residue using thermogravimetric analyzer under synthetic air atmosphere applying heating rates of 5, 10, and 15 °C/min, from room temperature to 900 °C. Three thermal decomposition stages were identified: dehydration (25.1–160 °C), oxidative pyrolysis (240–370 °C), and combustion (350–650 °C). The activation energies, reaction model, and pre-exponential factor were determined through four isoconversional methods, master plots, and linearization of the conversion rate equation, respectively. A scheme of two-consecutive reactions was applied validating the kinetic parameters of first-order reaction and two-dimensional diffusion models for the oxidative pyrolysis stage (149.57 kJ/mol, 6.97×10^{10} 1/s) and for combustion stage (77.98 kJ/mol, 98.61 1/s), respectively. The comparison between theoretical and experimental conversion and conversion rate showed good agreement with average deviation lower than 2%, indicating that these results could be used for modeling of guarana seed residue.

1. Introduction

In the isolated rural communities of Brazilian northern states present some problems related to energy supply. The extensive geographical area, long distances, natural obstacles, and poor access make difficult to assist the population. The implementation of alternative energy from renewable energy sources, such as solar, wind, hydroelectric, and biomass could be the energy solution for rural area. Among these resources, the biomass conversion through combustion could be advantageous due to the wide availability of material in the Amazon region (van Els et al., 2012; Sánchez et al., 2015).

The combustion is the main conversion process of biomass in energy. The volatile matter released from biomass thermal decomposition in oxidative atmosphere reacts leading the combustion of the carbon-based solid. During this process may occur simultaneously chemical reactions and transport phenomena between solid and gas phases (Jenkins et al., 1998; Anca-Couce et al., 2012). The determination of the reaction kinetics is very important for modeling combustion furnace in the industrial scale, in order to avoid energy loss and to reduce overall energy consumption (Chandrasekaran and Hopke, 2012).

Thermogravimetric analysis (TG) is the most commonly technique used to investigate the thermal decomposition kinetics of biomass. Different experimental conditions such as heating rate (1.25–50 °C), atmosphere (nitrogen, argon, synthetic air, and oxygen), and particle size (128–2000 μm) influence and affect the reaction kinetics (Fisher et al., 2002; White et al., 2011). Among these parameters, the atmosphere effect is one mostly discussed in the literature, in which can be characterized as inert for pyrolysis (Rueda-Ordóñez et al., 2015; Rueda-Ordóñez and Tannous, 2015; Baroni et al., 2015; Tinoco-Navarro, 2015) and oxidant for combustion studies (Ramajo-Escalera et al., 2006; Munir et al.,

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http://dx.doi.org/10.1016/j.biortech.2016.07.099
0960-8524/

2009; Cruz and Crnkovic, 2016; Rueda-Ordóñez and Tannous, 2016).

In order to estimate the kinetic parameters of biomass combustion, several mathematical approaches, such as model-free, model fitting, consecutive reaction scheme, independent parallel reaction scheme, and distributed activation energy model (Rueda-Ordóñez et al., 2015), were found in literature. The isoconversional methods are strongly recommended to determine the activation energy, and assist in the first guess for the more complex kinetic schemes (Vyazovkin et al., 2011).

In Table 1 are presented some studies applying the isoconversional methods of Friedman (1964), Ozawa-Flynn-Wall (Ozawa, 1965; Flynn and Wall, 1966), modified Coats-Redfern (Braun et al., 1991), and Vyazovkin (1997) for different biomasses.

Ramajo-Escalera et al. (2006) evaluated the decomposition kinetics of sugarcane bagasse through Vyazovkin method (Vyazovkin, 1997) considering a single global reaction (room temperature-600 °C). The average activation energies obtained for different conversion ranges were: (i) $\alpha = 0.02–0.05$ (76.1 kJ/mol) associated with dehydration, (ii) $\alpha = 0.15–0.60$ (333.3 kJ/mol) related to the combustion and carbonization, and (iii) $\alpha = 0.70–0.90$ (220.1 kJ/mol) corresponding to combustion.

Rueda-Ordóñez and Tannous (2016) studied the thermal decomposition kinetics of sugarcane straw (510 μm) applying the Vyazovkin method (Vyazovkin, 1997). These authors adopted strict temperature ranges for each reaction stage, disregarding moisture loss stage. The activation energies obtained for the two main stages, oxidative pyrolysis and combustion, were: (i) from 148 kJ/mol to 320.0 kJ/mol (150–350 °C), and (ii) from 352 kJ/mol to 159.0 kJ/mol (350–600 °C), respectively. Also, they observed that in synthetic air the thermal decomposition (up to 400 °C) occurred in a lower temperature range in respect to inert atmosphere (nitrogen). The activation energies of pyrolysis, determined by Rueda-Ordóñez and Tannous (2015), were equivalent to those in the oxidative pyrolysis conversion range between 0.05 and 0.85.

Cruz and Crnkovic (2016) compared the decomposition kinetics (room temperature-700 °C) of different biomasses (*tucumã* seed with almond, coffee husk, and rice husk), wherein the activation energies were obtained by the modified Coats-Redfern method. The authors considered three main decomposition reactions identified on the DTG curves through specific peaks such as: (i) hemicellulose, (ii) cellulose, and (iii) lignin. These biomasses present distinct compositions, thereby obtaining different activation energies ranges: *tucumã* seed (75–300 kJ/mol), coffee husk (21–190 kJ/mol), and rice husk (65–145 kJ/mol).

Also, in Table 1 is observed that the activation energy related to the thermal decomposition in inert atmosphere varied between 142 and 171 kJ/mol for several biomasses (Rueda-Ordóñez et al., 2015; Rueda-Ordóñez and Tannous, 2015; Baroni et al., 2015; Tinoco-Navarro, 2015). However, concerning the reactions in oxidative atmosphere, a wide range of activation energy was observed from 50 to 352 kJ/mol for main stages.

In search of other sources of biomass for energy purposes in the Amazon region was found the residue of guarana seed. The richest part of guarana fruit for consumption is the seed. After extraction of interest components (e.g., methylxanthines, including caffeine,

Table 1
Activation energy of several biomass obtained by isoconversional methods.

Reference	Biomass	$\bar{d}_p$ (μm)	TG condition	Atmosphere	Activation energy (kJ/mol)			
			Sample mass (mg) Heating rate (°C/min) Temperature range (°C)		FD[a]	OFW[b]	MCR[c]	VZ[d]
Ramajo-Escalera et al. (2006)	Sugarcane bagasse	–	1-2 5, 10, 20 RT[e]-600	O_2	–	–	–	1st S[f]: 0–76 2nd S[f]: 330–350 3rd S[f]: 200–220
Baroni et al. (2015)	*Tucumã* endocarp	499.4	10,18 5, 10, 20 RT[e]-900	N_2	160.5	147.3	144.6	145.0
Rueda-Ordóñez and Tannous (2015)	Brazil nut woody Shell	499.0	10,06 5, 10, 20, 40 RT[e]-900	N_2	144.5	145.7	142.7	–
Tinoco-Navarro (2015)	Sapucaia nut woody shell	497.3	10,0 5, 10, 20, 40 RT[e]-900	N_2	171.2	149.6	147.0	–
Rueda-Ordóñez and Tannous (2015)	Sugarcane straw	510.0	3,0 1.25, 2.5, 5, 10 RT[e]-900	N_2	163.4	–	–	–
Cruz and Crnkovic (2016)	*Tucumã* seed	460	10 10, 15, 20, 25, 30 RT[e]-700	Synthetic air N_2/O_2 (80/20)	–	–	1st S[f]: 75–85 2nd S[f]: 50–270 3rd S[f]: 110–300	
	Coffee husk	460					1st S[f]: 21–175 2nd S[f]: 115–190 3rd S[f]: 80–95	
	Rice husk	460					1st S[f]: 65–70 2nd S[f]: 95–145 3rd S[f]: 125–135	
Rueda-Ordóñez and Tannous (2016)	Sugarcane straw	510.0	3,0 2.5, 5, 10 RT[e]-900	Synthetic air N_2/O_2 (80/20)	–	–	–	1st S[f]: 148–310 2nd S[f]: 160–352

[a] Friedman method.
[b] Ozawa-Flynn-Wall method.
[c] Modified Coats-Redfern method.
[d] Vyazovkin method.
[e] RT: room temperature.
[f] S: thermal decomposition stage.