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KINECT STUDY OF SUGARCANE BAGASSE COMPOUNDS IN INERT AND OXIDANT ATMOSPHERE

Miriam Ricciulli de Oliveira
Gretta Larisa Aurora Arce Ferrufino
Carlos Dias Maciel
Ivonete Ávila
UNESP – São Paulo State University, Guaratinguetá Engineering Faculty, Department of Energy, Combustion and Carbon Capture Laboratory (LC_3), Av. Dr. Ariberto Pereira da Cunha, 333, 12.516-410, Guaratinguetá-SP, Brazil.
miriamrdo@yahoo.com.br, grettagaf@yahoo.es, ivonete.avila@unesp.br

Abstract. *Biomass has been shown to be an important source of renewable and sustainable energy, which can be obtained from agro-industry residues. This work focus on carry out a kinetic study of the chemically isolated components of sugarcane bagasse through the TGA/DTG curves in an oxidizing atmosphere (20%O_2 and 80%N_2) and in an inert atmosphere (N_2). The thermogravimetric tests were carried out in the temperature ranging from 30 to 900°C, with heating rates of 10, 20 and 30°C/min for both atmospheres. The data obtained from the curves were applied in the mathematical model KAS (Kissinger-Akahira-Sunose), which allowed to determine the activation energy for different degrees of conversion of each isolated component of the biomass in both atmosphere. Theses results contribute to better understand the mechanisms of conversion of biomass compounds and to improve the efficiency of the conversion processes.*
Keywords: *Biomass, TGA, Surgacane Bagasse, Kinetics analysis.*

1. INTRODUCTION

Due to the environmental impact caused by the use of fossil fuels in energy generation, biomass has been emphasised as an alternative energy source, because it is clean, renewable, and abundant in the environment, and can also being obtained from agro-industrial residues, demonstrating itself as an important model of sustainable energy (NIMMANTERDWONG; CHALERMSINSUWAN; PIUMSOMBOON, 2021; XU et al., 2020). It can be converted into fuel by thermal conversion processes such as pyrolysis, gasification and combustion and the efficiency of these processes depends on it composition and physicochemical properties which vary according to the species and part of the plant used (CHEN et al., 2020). Due to this variability, it is important to perform an accurate characterization of the material(NIMMANTERDWONG; CHALERMSINSUWAN; PIUMSOMBOON, 2021).

Lignocellulosic biomass consists mainly of cellulose, hemicellulose and lignin and small amounts of pectin, protein, extractives and ash (QUAN; GAO; SONG, 2016). Cellulose is the most abundant component of biomass, formed by long chains glucose monomeric units connecting via β-glycosidic linkages, while the lignin is a hydrophobic polymer composed of several cross-linked polymer of phenolic substances (HO; ONG; WU, 2019).

The main components can be isolated by different chemical treatments promoting the breakdown of biomass polymeric matrix, such as the bleaching process with uses hydrogen peroxide in an alkaline medium and the process of organosolv pulping(HO; ONG; WU, 2019).

Thermogravimetric analysis is commonly used to analyze the thermal behavior of biomass and its constituents, simulating the conversion processes, obtaining a curve that records the mass loss over time (TGA) and the derivative of this curve (DTG) (KUMAR et al., 2021).

Kinetic modeling for conversion process is essential for an accurate Study of kinetics reaction of thermochemical conversions process is important to prediction of its behavior under various operating conditions promoting efficient design, scale-up, and operation (CHEN et al., 2020; SHARMA et al., 2023). Thermogravimetric analysis is a technique commonly used in kinetic studies of biomass decomposition, in which mass loss curves are generated in relation to temperature or time, which, in addition to helping to estimate the devolatilization stages of the main constituents of lignocellulosic biomass, allow the determination of kinetic parameters, such as activation energy (Eα) (SHARMA et al., 2023).

This work focus on carry out a kinetic study of the chemically isolated components of sugarcane bagasse through the TGA/DTG curves in an oxidizing atmosphere (20%O_2 and 80%N_2) and in an inert atmosphere (N_2). The thermogravimetric tests were carried out in the temperature ranging from 30 to 600°C, with heating rates of 10, 20 and 30°C/min for both atmospheres. The data obtained from the curves were applied in the mathematical model KAS (Kissinger-Akahira-Sunose), which allowed to determine the activation energy for different degrees of conversion of each isolated component of the biomass in both atmosphere.

2. MATERIALS AND METHODS

This study was carried out at the Laboratory of Combustion and Carbon Capture and at the Laboratory of Biomass Characterization, that belong to the Department of Chemistry and Energy, at Unesp in Guaratinguetá.

2.1 Raw material preparation

The sugarcane bagasse was supplied by the company Raízen, being washed with running water and then left immersed in water at 50 °C for one hour, in order to remove impurities contained in the biomass. The biomass was then dried in an oven at 100 °C for 48 hours, and then it was ground and sieved at 18 mesh, using a Willye-type knife mill, thus obtaining the biomass *in natura*.

2.2 Lignin extraction

For the isolation of lignin, the acetosolv pulping process was used, where the biomass was treated with 93% acetic acid (w/w) in the proportion biomass/solvent 1:10 (w/v), using hydrochloric acid 0.3% (w/w) as a catalyst (BENAR, 1992). The biomass and reagent mixture were heated to 110 °C in a round bottom flask, placed in a glycerol bath and connected to a reflux condenser with water at room temperature. After reaching the temperature, the system was kept under stirring and constant temperature for 2 h. After this time, the mixture was filtered and the solid was washed with distilled water in order to neutralize it and then taken to an oven where it was dried at 60 °C for 24 hours, obtaining a delignified biomass. The filtrate was concentrated in a rotary evaporator at 80 °C and then distilled water was added at 80 °C in a ratio of 1:10 (v/v), precipitating the lignin. The mixture was allowed to stand for 24 hours, being then filtered and washed abundantly with deionized water. The lignin recovered was dried in an oven at 60°C for 24 hours.

2.3 Cellulose extraction

The delignified biomass obtained in item 2.1 was subjected to the bleaching process in order to remove the hemicellulose and lignin still present in the biomass. The process was carried out at 80 °C with constant constant for one hour, in the proportion of 5 g of biomass for each 100 mL of H_2O_2 24% (v/v) and 100 mL of NaOH 4% (m/v) (OLIVEIRA et al., 2016). The mixture was then filtered and the solid was washed with distilled water until neutral pH and dried in an oven at 60 °C for 24 hours, thus obtaining cellulose.

2.4 Thermogravimetric analysis

The thermal analysis of the cellulose and lignin samples was performed by an SDT 600 thermoanalyzer (TA Instruments), in an inert (N_2) and oxidizing atmosphere (20%O_2 and 80%N_2), obtaining the TGA/DTG curves. The tests were carried out under the following experimental conditions: volumetric flow rate of 100 mL/min of carrier gas, sample mass of (5±0.2) mg and heating rate of 10, 20 and 30 °C/min from a temperature of 30 °C to 900 °C.

2.5 Kinetic study

In this kinetic study, the activation energy (Ea) was determined as a function of the degree of conversion (α) using the mathematical model KAS (Kissinger-Akahira-Sunose), which is an isoconversional technique to determine Ea of a reaction with different degrees of conversion, without pre-setting a reaction model (GALINA et al., 2019).

The degree of α conversion is determined as a function of the sample's mass loss, as shown in Eq. (1), where w_f is the final mass of the sample, w_o is the initial mass and w is the mass recorded over the reaction time.

$$\alpha = \frac{w - w_0}{w_f - w_0} \tag{1}$$

The determination of the activation energy as a function of the degree of conversion is given by Eq. (2), where T is temperature, R is the universal gas constant, A and Eα are Arrhenius parameters, β is the constant heating rate applied to the reaction, and g(α) is the overall reaction model.

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R_\alpha}.\frac{1}{T_\alpha} \tag{2}$$

For each α conversion value, plot ln(β/T_α^2) versus 1/Tα to obtain a line whose slope is –Eα/R. The pre-exponential factor (A) is obtained through calculations that depend on the intercept of the extrapolation of the straight line on the y axis, thus both Eα and A are obtained as a function of the conversion (α).

3. RESULTS AND DISCUSSION

Initially, the TGA/DTG curves obtained were analyzed to define the range from ignition temperature to burnout temperature for the 3 heating ratios. The interval between the ignition and burnout temperatures is the interval where sample decomposition occurs, both in an inert and oxidizing atmosphere.

The temperature ranges defined for the cellulose and lignin samples in an inert and oxidizing atmosphere are described in Table 1.

Table 1. Temperature intervals used in the kinetic study

Sample	Temperature Range (°C)					
	Inert Atmosphere			Oxidizing Atmosphere		
	10 °C/min	20 °C/min	30 °C/min	10 °C/min	20 °C/min	30 °C/min
Cellulose	161 - 630	181 - 626	192 - 674	175 - 466	180 - 500	192 - 517
Lignin	127 - 810	144 - 804	142 - 795	165 - 477	152 - 529	155 - 551

The initial degradation temperature of cellulose was higher than lignin due to its regular structure, formed by basic cellobiose units, with good thermal stability (FAN et al., 2017). Liginin is formed by 3 basic units (guaiacyl, syringyl and p-hydroxyphenyl) and many hydroxy and methoxy side chain radicals, which have a low binding energy, starting their decomposition at a lower temperature than cellulose (FAN et al., 2017). During the decomposition reaction in an inert atmosphere, mainly the cleavages of side chains and ether bonds, leading to decomposition over a wide temperature range (FAN et al., 2017). It should be noted that the higher the temperature at which decomposition begins, the greater the activation energy required for the reaction to occur (FAN et al., 2017).

It is observed in Table 1 that the reaction in an oxidizing atmosphere occurs more quickly, finishing earlier than in an inert atmosphere. This occurs because during the devolatilization reactions and thermal degradation of the sample, the residual organic part of the sample occurs (BRACHI et al., 2019).

Figure 1 illustrates the conversion behavior as a function of temperature for cellulose and lignin.

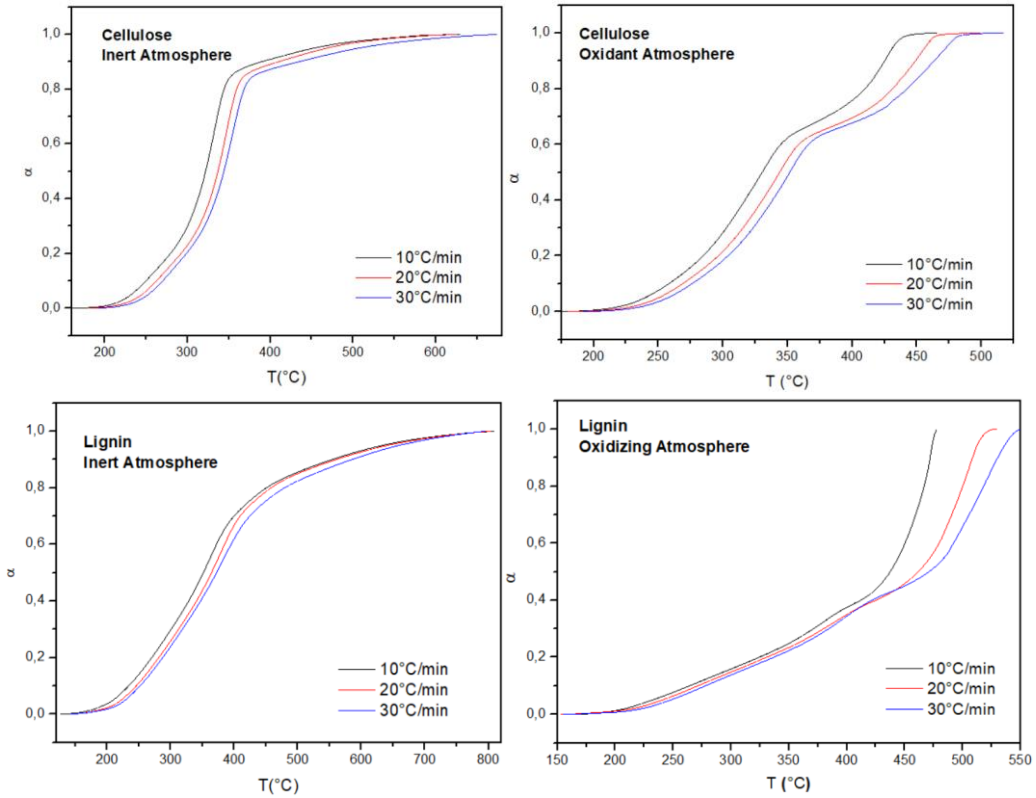

Figure 1. Conversion rate as a function of temperature for cellulose and lignin in inert and oxidizing atmospheres

It is verified that the conversion of cellulose and lignin followed the sequence of occurrence according to the heating ratio for both atmospheres. The exception occurred for the lignin sample in an oxidizing atmosphere, since the heating curve for the rate of 30 showed a different conversion behavior from the temperature of 375°C until 475°C overlaps the 20 °C/min curve, probably due to the high reactivity of the sample in this temperature range. The increased oxygen concentration can lead to increased decomposition rate due to environmental reactivity (LOPES; PEREIRA; TANNOUS, 2018).

It is observed that in an inert atmosphere the sample decomposes mainly between 200 and 400 °C (devolatilization stage), with around 80% conversion to cellulose and 60% conversion to ligin in this temperature range. In an oxidizing atmosphere, there is an increase in sample conversion after a temperature of 400 °C, due to the oxidation reactions of the carbonaceus materials and minerals that did not react in the devolatilization stage (LOPES; PEREIRA; TANNOUS, 2018).

The profiles of the activation energy variation (Eα) as a function of the conversion (α) of each component is illustrated in Fig. 2.

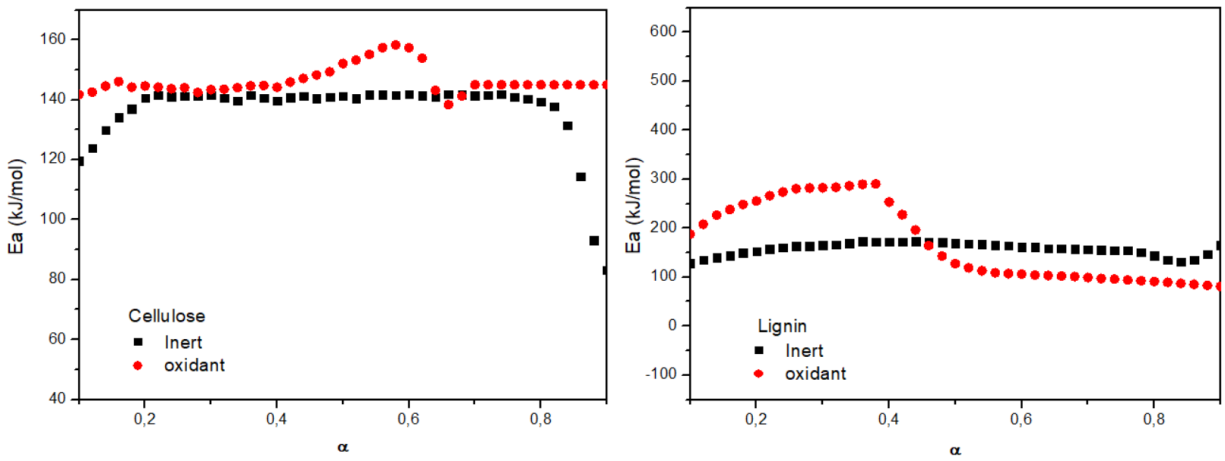

Figure 2. Activation energy as a function of temperature for cellulose and lignin in both atmospheres

It can be seen that for cellulose and lignin, the Ea required for the reaction in an inert environment did not vary significantly during most of the conversion, maintaining a stable value from 20 to 80% of conversion.

The Eα values showed greater variability as a function of the degree of conversion in an oxidizing environment, when compared to the values obtained in an inert environment. Cellulose had the highest Ea value around 58% conversion. Lignin obtained an EA peak around 38% of conversion, decreasing the value throughout the reaction. According to Lopes, Pereira e Tannous (2018) as lignin is a complex polymer that decomposes over a wide temperature range, its activation energy is not usually determined by isoconversional methods, as it does not present a specific decomposition peak. When there is a difference of more than 30% between the minimum and maximum activation energy values, it is necessary to apply kinetic models that take independent parallel reactions into account (LOPES; PEREIRA; TANNOUS, 2018).

The avarage of values of activation energy (Ea) for conversion rates of celulose and lignin in inert and oxidizing environments obtained from the KAS method are presented in Table 2. It is noted that the values obtained are close in both environment, but the activation energy values are higher in oxidizing environment.

Table 2. Average activation energy values obtained for both atmospheres

Sample	Ea (kJ/mol)	
	Inert	Oxidant
Cellulose	140,87	146,29
Lignin	160,01	169,92

It should be noted that the quoted values correspond to the average of values between 10 and 90% of conversion and that they are close to the values cited in the literature (QUAN; GAO; SONG, 2016).

It should be noted that the hemicellulose ea was not determined in this study, due to the difficulty in isolating a sample with a high hemicellulose content.

4. CONCLUSIONS

With this research, the mathematical model KAS proved to be effective for determining the activation energy for the cellulose and lignin components, isolated from sugarcane bagasse during pyrolysis, finding values close to those reported in the literature. The activation energy values obtained are coherent, because the greater the structural stability of the component, the greater the thermal stability, therefore the greater the energy spent to decompose the material.

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