Pyrolytic Degradation Studies of *Acacia mangium wood*

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Pyrolytic degradation of *Acacia mangium* wood was studied. The chemical composition of biomass, immediate and elemental analyses and calorific value for biomass and char, were determined. The standard and the derivative curve thermogravimetric analysis (TGA and DTG) were obtained. Devolatilization maximum of values between 250±20 °C and 380±20 °C were observed, with completion after 2 h, which confirms the selection of 2 hours for pyrolysis. Kinetic study was performed at different heating rates for a conversion rate from 20% to 80%. Average values of activation energy for temperature in degrees K of 228.57 kJ/mol for Biomass 1 and 199.36 kJ/mol for Biomass 2 were obtained by the isoconversion method of FWO. The lower value of activation energy for Biomass 2 was related to the possible catalytic activity of ash. The values of correlation coefficient from 0.9418 to 0.9946 for Biomass 1 and from 0.8706 to 0.9918 for Biomass 2, indicate the reliability of the first-order reaction model. The caloric values obtained were: Biomass 1 (16962 kJ/kg), Biomass 2 (16974 kJ/kg), chars from Biomass 1 (between 23731 y 26 942 kJ/kg) and gas from Biomass 1 and Biomass 2 (3858.7 and 4859.4 kJ/m^3, respectively).

Keywords: Analysis; Biomass; Kinetic; Pyrolysis; Thermogravimetry

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INTRODUCTION

The *Acacia* genus, one of the most important of the Fabaceae family (subfamily Mimosaceae), includes about 1200 species. This genus is abundant in tropical and subtropical regions of the world such as Australia, Africa, India, and America (Simmons 1987) and the *Acacia* plantations are in wide development in rural Cuban territory. It is a fast growing tree and is often chosen for the reforestation and restoration of desert lands. Its total biomass can increase from 1.8 t.ha^{-1} (year 1), to 5 t.ha^{-1} (year 3), to 10.9 t.ha^{-1} (year 5) (Shanmugavel and Francis 2001).

Agricultural residues, forestry residues as well as wood, are important sources of energy (Apaydin *et al.* 2007). To use biomass to best advantage as an energy source, a previous study of chemical composition, immediate analysis, elemental analysis, and kinetic study from thermal degradation of the material is necessary. The chemical composition of biomass can be regarded as two groups of substances: 1) extractable components of the cell wall and 2) cellulose, hemicellulose, and lignin according to Márquez *et al*. (2002).

In the pyrolysis process, the temperature range from 250 to 350 °C is very important because most thermal decomposition of hemicellulose and cellulose takes place in this range with wood (ASTM D 1106-96 2007; ASTM D 3172-07 2007; García *et al.* 2009; Ju *et al*. 2009; Gurten *et al.* 2012; Wang *et al.* 2014). The main decomposition reaction consists of the breakdown of the glycosidic linkages and the consequent partial depolymerization of the cellulosic components of wood. In this stage, the decomposition of lignin is initiated. The formation of carbonaceous products of high molecular weight begins above 300 °C (ASTM D 3173-87 2003). The pyrolysis processes can be developed at different heating rates, distinguishing the slow pyrolysis, fast pyrolysis, and flash pyrolysis; the amount of solid, liquid, and gaseous substances obtained depends on the type of pyrolysis developed (Brossard 2003; Amutio *et al.* 2011; Klug 2012). If pyrolysis is slow, the product obtained in larger quantities is char, which can be used to obtain energy and to obtain activated carbons. The char can be obtained at laboratory furnaces or larger scale, and their caloric values are close to 30 kJ/g (Márquez *et al*. 2001), meanwhile, the gases are preferably obtained by the method of gasification where caloric values are ± 5000 kJ/m^3 (Demirbas 2001b, Aguiar *et al.* 2013). The calorific value is an important index of the quality of fuels, including biomass. The high calorific value, defines the energy content of a fuel, while the low caloric value defines its net calorific value. The caloric value can be determined experimentally in a calorimeter, also by well established equations (Demirbas 2000; Maiti *et al*. 2007; Bhavanam *et al.* 2015).

There are many methods for the non-isothermal analysis of the solid state, from kinetic data; these methods can be divided into two types: methods to model fitting and model-free methods (isoconversional) (Masnadi *et al.* 2014; Myung *et al.* 2014). The isoconversional methods require multiple kinetic curves for the analysis; estimates of several curves at different heating rates are achieved in the same conversion value, which allows to calculate the activation energy for each point conversion. Repeating this procedure in different conversion values, a profile of the activation energy is obtained as a function of conversion (Hu *et al.* 2007; Sánchez *et al.* 2009; Slopiecka *et al.* 2012; Myung Jeong *et al.* 2014; Ceylan and Topcu 2014).

The aim of this work was to perform a thermogravimetric study of acacia wood, which includes kinetic analysis using the free model isoconversional Flynn, Wall, and Ozawa (FWO) of order 1 (Slopiecka *et al.* 2012; Myung, *et al*. 2014, Ceylan and Topcu 2014). By carrying out an experimental kinetic study of the pyrolysis of *Acacia* and the yields of the resulting carbonaceous solid and liquids, the energetic potential of the raw material was determined.

EXPERIMENTAL

Biomass Sample

Woody biomass of *Acacia mangium* Willd from the province of Pinar del Río, Cuba, was used. A selection of young trees between 3 and 5 years old was conducted in an artificial forest. The floor was a skeletal type of sandy loam. Five parcels of 500 m^2 were defined and five trees, each with similar morphological characteristics, were selected from each parcel (TAPPI Standard T-257-cm-85 (TAPPI 1998). Wood with bark

(Biomass 1) and wood without bark (Biomass 2) were selected and crushed. Particles between 0.5 and 1.6 mm in size were chosen for the study.

Chemical Composition

Chemical and physicochemical properties were determined according to the following international standards:

Lignin: ASMT D 1106-96 (2007) TAPPI T- 257-cm-85 (1998)

One gram of sample (free removable) was placed in an Erlenmeyer flask, adding 15 mL of 72% sulfuric acid solution. The formed mixture was stirred for 2 h at interval and later transferred to a ball, adding it to distilled water to a concentration of 3% solution. This was boiled under reflux for 4 h. Finally the solid was filtered. Lignin free acid was washed with hot water and dried in an oven at temperature of 60 ° C, then weighed to constant mass.

Cellulose: TAPPI Test Method T 203 os-74

The test sample was placed in a glass of 300 mL, and 75.0 mL of NaOH was added with 17.5% concentration. The pulp was agitated to full dispersion. When the pulp had been dispersed, the pulp fibers bonded with a glass rod were removed. The stirrer with 25.0 mL of the NaOH solution was washed, now having 100.0 mL of reagent added to the pulp. The pulp slurry was stirred with a rod and in a bath at 25 ± 0.2 ° C. After a period of 30 min from the first addition of reagent NaOH, 100.0 mL of distilled water was added at 25 ± 0.2 °C to the pulp suspension and stirred thoroughly with a rod. The beaker was left in the bath for a further period of 30 min so that the total extraction time was 60 ± 5 min. At the end of the 60-min period, the pulp suspension was stirred with a rod and transferred to a filter funnel. The first 10 mL of filtrate was discarded, then about 100 mL of filtrate was collected in a clean dry flask filtration. 25.0 mL of the solution and 10.0 mL of 0.5 N potassium dichromate solution was pipetted into a 250 mL flask. Then 50 mL of concentrated H_2SO_4 was slowly added while the flask was stirred. The hot solution was left for 15 min, then 50 mL of water was added and cooled to room temperature. Next 4 drops of ferroin indicator were added and titrated with 0.1 N solution of ferrous ammonium sulfate to a purple color.

Total hemicelluloses were estimated as the difference between 100% and the sum of the percentages of cellulose and lignin in the wood that was free of extractables (Carballo *et al*. 2004, with eucalyptus wood).

Moisture: ASTM D 4442-07 (2007)

Five grams of sample were placed in a ceramic crucible. The crucible with the sample was placed in a muffle furnace at 103 °C for a period of 3 h.

Ash: ASTM D 1102-84 (2007)

Five grams of sample, free of moisture were placed in a ceramic pot. The crucible with the sample was placed in a muffle furnace at 600 °C for a period of 3 h.

Volatiles according to ASTM D 3175-07 (2007)

One gram of sample, free of moisture was placed in a ceramic pot. The crucible with the sample was placed in a muffle furnace at 950 °C for a period of 7 min. The fixed carbon was determined by difference, minus the ash.

Thermogravimetric Analysis

TGA analysis and differential thermogravimetric analyses (DTG) were carried out in a modular pattern, using a mechanical device, the RB-3000-20, from BP Engineering, which was provided with a tubular furnace electric alumina core reaching a maximum temperature of 1200 °C. Analyses were carried out using an electronic balance with sensitivity to 0.001 g, nickel crucible, type K thermocouple, temperature programmer, and a microprocessor for data acquisition.

To determine the thermal decomposition integral curve, experiments were performed in thermobalance, studying the variation of the final conversion subject to the heating rate. The sample was heated to 900 °C and time, temperature, and weight data were recorded during the heating period (Aguiar *et al*. 2008, with shell citric). As study variables, heating rates of 5 °C/min, 10 °C/min, and 15 °C/min were selected. Nitrogen, with a flow rate of 100 mL/min, was used as an inert gas (Park *et al.* 2013, with pine chips). The experimental data recorded for the dynamic experiments included the transformation of mass, time, and temperature.

During the thermal decomposition of the biomass, the degree of conversion (X) was studied in relation to time by the following equation,

$$X = \frac{m_0 - m_i}{m_0} 100 \tag{1}$$

where X is the conversion (%) (the degree of conversion changes from an initial value (0) to a final value (X), m_0 is the initial biomass mass (mg), and m_i is the mass (mg) of the biomass at time i. The highest conversion is obtained from Eq. 2,

$$X = \frac{m_0 - m_f}{m_f} \tag{2}$$

where m_f is the final mass of biomass.

The mass fraction (f) and the conversion α were defined as in Eqs. 3 and 4,

$$f = \frac{m_i}{m_0} \tag{3}$$

$$\alpha = \frac{m_0 - m_i}{m_0 - m_f} \tag{4}$$

where m_f is the final mass, at T= 800 °C

The mass loss is defined in Eq. 5, as follows:

$$\frac{d\alpha}{dt} = kTf(\alpha) \tag{5}$$

where $f(\alpha)$ represents the reaction model, $k(T)$ (rate constant as a function of temperature) is the rate constant as expressed by the Arrhenius Law as $k(T)=A\exp(-E_a/RT)$ (Slopiecka *et al*. 2012; Ceylan and Topcu 2014; Shadangi and Mohanty 2014).

If $f(\alpha)$ is $(1–\alpha)n$, where n is the reaction order, Eq. 5 then takes the form described in Eq. 6 for the different conversions of individual reactions, as proposed by other authors (García *et al*. 2010; Syed *et al*. 2011; Slopiecka *et al*. 2012),

$$\frac{dX}{dt} = k\left(A_s - X\right)^n \quad \text{or} \quad \frac{d\alpha}{dt} = k(1-\alpha)^n \tag{6}$$

where k is the Arrhenius reaction rate constant.

$$k = Z * e^{-Ea/RT} \tag{7}$$

In Eq. 7, Z is the frequency factor (s^{-1}), E_a is the activation energy (kJ/mol), R= 8.3143 J/mol*K (the universal gas constant), and T is the temperature (K).

The calculation of the frequency factor in the dynamic experiments was based on isoconversional methods (Lyon 1997; Hu *et al*. 2007; Sánchez *et al.* 2009; Jiang *et al.* 2014), as follows (Eq. 8),

$$Z = \frac{B \; *\left(E_a + 2 * R * T_\alpha\right) * e^{E_a / RT\alpha}}{R * T_\alpha{}^2} \tag{8}$$

where B is the heating rate in °C/min, and T_α is the temperature (K) at which the maximum conversion is achieved.

Determination of Volatiles in the Thermogravimetric Balance

Tar and gas products were collected in a system consisting of a trap bottle to collect the liquid fraction of one cleaning system (electrostatic precipitator capacitors and filters), leads, and a vacuum system. Nitrogen was used as the purge gas. The study was conducted with a non-isothermal analysis, then the heating rate was 10 °C/min. to 900 ºC.

The liquid fraction of tars and water retained in the capacitor and the electrostatic system were collected using isopropanol. After the liquid fraction was extracted and filtered, a qualitative analysis was performed on a gas chromatograph GC-MS with the following operating conditions:

- Column HP-5MS 5% phenyl methyl siloxane
- Initial Temperature: 40 ºC
- Heating rate: 10 ºC/min.
- Final Temperature: 280 °C
- Spectra library: Wiley275.

To calculate the percentage of gases, the average area of gases were multiplied by the percentage concentration patterns, and the product was divided by the area of the pattern. Subsequently, the percentage of each gas was calculated from the total gas volume. Multiplying each percentage of gas by its specific calorific value and summing all values, the lower caloric value in kJ/m^3 for total gas was obtained.

Study of the Pyrolysis in the Furnace

Pyrolysis experiments in a vertical furnace of 8 cm inner diameter and 30 cm in length were performed. A quartz tube located on the inside of the furnace was used as a reactor. The sample was placed in a ceramic holder inside the quartz tube. A nitrogen flow of 150 mL/min was used as carrier gas. According to the results obtained in the thermobalance, pyrolysis temperatures of 400 °C, 450 °C, and 500 °C were selected. The heating rate was 10 °C/min and the residence time of the sample in the furnace was 2 h (Márquez *et al*. 2002, with citric shell; Cordero *et al*. 2001, for pine and eucalyptus wood). The obtained char samples, AW40010, AW45010, and AW50010, were named according to the following conventions: "AW" indicates *Acacia* wood, followed by the pyrolysis temperature and heating rate. For example, a sample of *Acacia* wood with bark was pyrolyzed at 450 ºC, so the obtained carbon was named AWB45010-2. The char and raw material were characterized by immediate analysis, elemental analysis and heating value determination.

Moisture levels were determined according to ASTM D 3173-87 (2003). 1 g sample was placed in a ceramic crucible. The crucible with the sample was placed in a muffle furnace at 110 °C for a period of 30 min.

The ash was determined according to ASTM D 3174-04 (2004): 1 g sample was placed in a ceramic crucible. The crucible with the sample was placed in a muffle furnace at 700 °C for a period of 2 h.

Volatiles were evaluated according to ASTM D 3175-07 (2007): 1 g sample was placed in a ceramic crucible. The crucible with the sample was placed in a muffle furnace at 900 °C for a period of 7 min.

The fixed carbon was determined by difference minus the ashes according to D 3172-07 ASTM (2007). The elemental analysis (C, H, N; O by difference) was determined on a Perkin-Elmer, model 240 °C. For determining the calorific value, pellets were prepared with a volume of approximately 2 cm^3. This was accomplished via the compression of 1 g of biomass and 2 g of char at a pressure of 80 kPa. A calorimetric bomb was used, according to the standard ASTM D5865–10 (2010).

RESULTS AND DISCUSSION

Chemical Composition and Thermal Gravimetric Analysis

Table 1 shows the results of chemical and physicochemical biomass characterization.

Table 1. Chemical Composition. Proximate and Elemental Analysis (% db)

	Biomass 1 (wood without bark)	Biomass 2 (wood with bark)
Lignin (%)	27.18	29.08
Cellulose (%)	48.44	42.11
Hemicellulose	23.93	28.03
Moisture (%)	10.5	11.7
Proximate analysis (% mf)		
Ash	0.45	0.78
Volatiles	88.3	82.43
Fixed carbon	11.3	16.8
Elemental analysis (% mf)		
Carbon	47.37	45.45
Hydrogen	6.06	6.60
Nitrogen	1.11	0.23
Oxygen**	45.46	48.02
HHV (kJ/kg)	16 962	16 974

** Oxygen is determined by difference

A correlation between lignin and cellulose values with volatile and fixed carbon values was observed. These results also correlate with calorific values studied in timber and are within the range of results obtained by Cordero *et al*. (2001) for pine and eucalyptus wood, Wang *et al*. (2009) with wheat and corn straw products, Márquez *et al*.

2009), with wood de Jambolán (*Syzygium Cuminii*), Nirmal *et al*. (2011) with several forest species, Kieseler *et al*. (2013) with poplar wood, straw, and grass, and Aguiar *et al*. (2013) with solid residue the orange industrial process. When comparing the percentage of fixed carbon and volatile matter among both biomasses, a larger percentage of fixed carbon and a smaller percentage of volatile matter was observed in Biomass 2; this results from the influence of the ash in the formation of the carbonaceous solid (Raveendran *et al.* 1995, on influence of ash in different kinds of biomass). High lignin and hemicellulose values indicate a larger quantity of carbon fixed, and high values of volatiles that assure the quick ignition of the wood and the char; on the other hand, the percentage of ash in Biomass 1 diminished energy consumption in the secondary reactions, as it was the possible cause of the higher heating value. The dynamic TGA and DTG experiments are shown in Figs. 1 and 2 (Biomass 1) and Figs. 3 and 4 (Biomass 2).

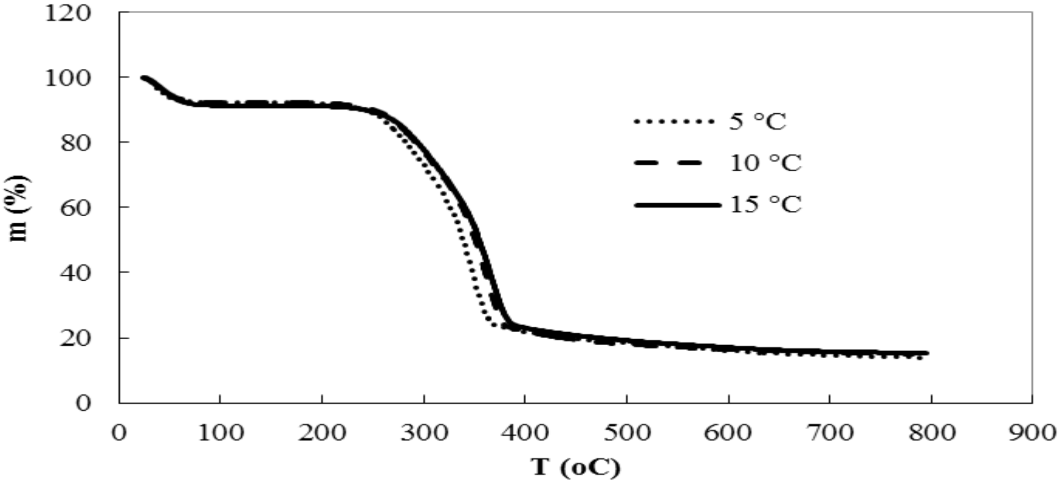

Fig. 1. Mass loss from thermal decomposition (TGA) of Biomass 1 (wood without bark) at heating rates between 5 and 15 °C/min.

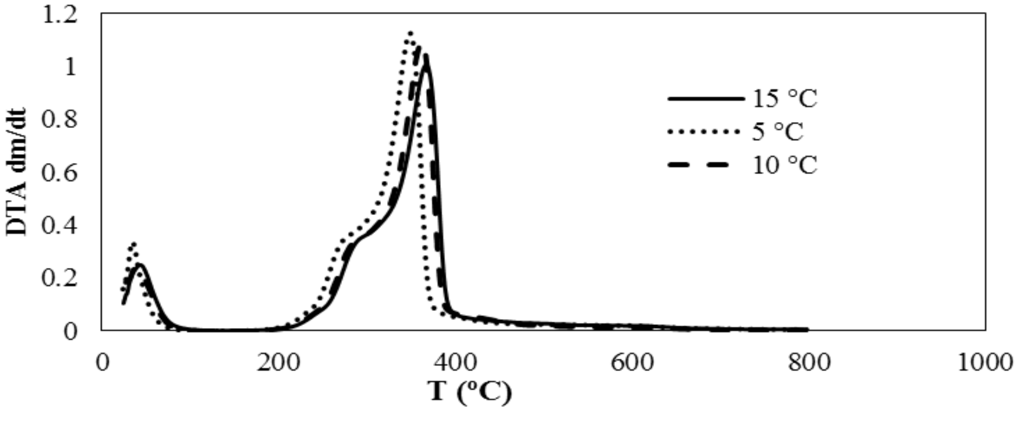

Fig. 2 Variation in the instantaneous rate of reaction with temperature at heating rates between 5 and 15 °C/min for pyrolysis (DTG) of Biomass 1 (wood without bark)

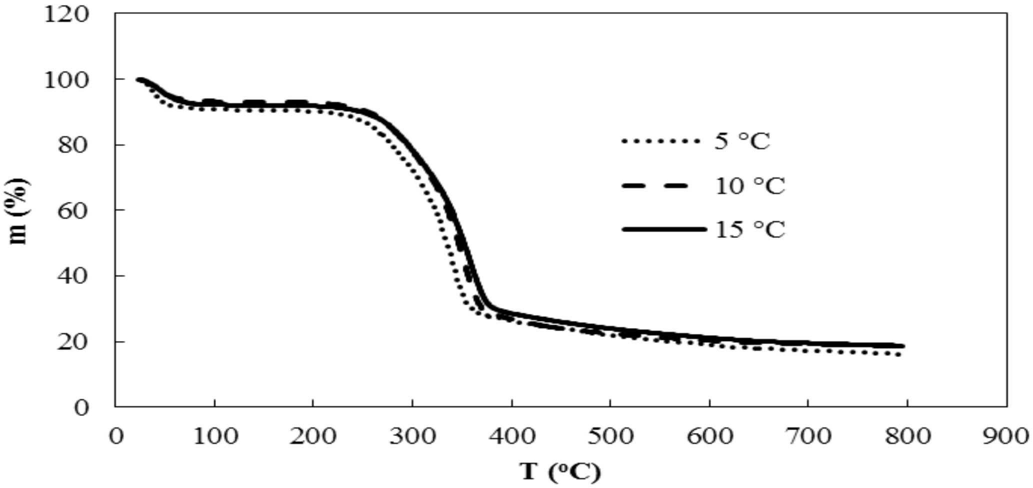

Fig. 3. Mass loss from thermal decomposition (TGA) of Biomass 2 (wood with bark) at heating rates between 5 and 15 °C/min

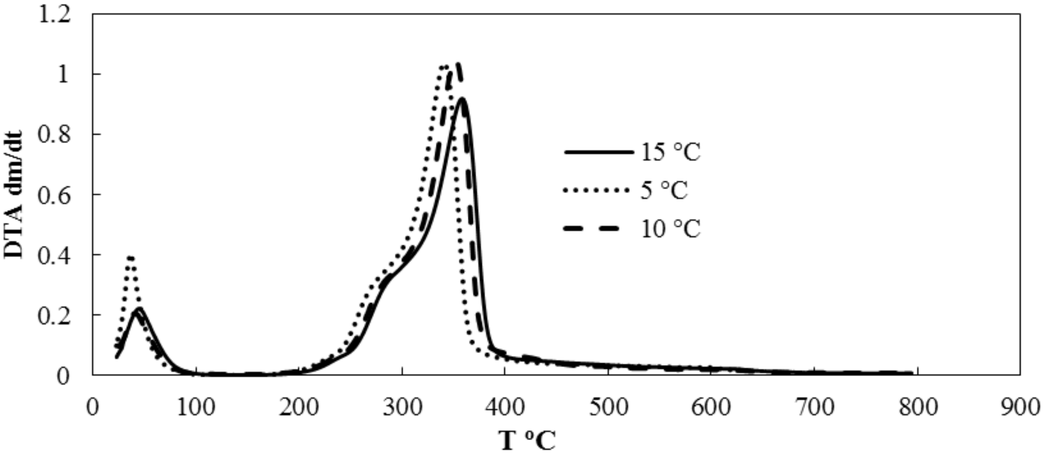

Fig. 4. Variation in the instantaneous rate of reaction with temperature at the heating rates between 5 and 15 °C/min for pyrolysis (DTG) of Biomass 2 (wood with bark)

Three distinct stages are part of thermal decomposition according to the chemical and physicochemical composition of the materials studied: lignin, cellulose, hemicellulose, volatile, ash, and fixed carbon (Skodras *et al*. 2007, with animal derived byproducts; Park *et al.* 2013 with pine chips containing bark). Figures 1 and 2 show a volatilization maximum identified between 250±20 °C and 380±20 °C, although sloping is somewhat prolonged.

At 200±20 °C, between 10% and 15% by mass was converted, corresponding to the first stage (water and extractables). The peaks appearing in Fig. 2 and 4 confirm this degradation step; similar results have been reported by Miranda *et al.* (2009) with sweet orange dry peel, Seong and Oladiran (2009) with switchgrass, Shen *et al*. 2009 with aspens, birch, oak and pine, and García *et al*. 2010 with *Leucaena leucocephala* and two composts with different maturation levels. The second stage temperature range was from 250±20 °C to 325 °C, at which the most volatiles decomposed, mainly hemicellulose and cellulose accounting for about 60 to 70 % of the total mass. An incipient peak may be observed in Figs. 2 and 4, and this may correspond to the stage of degradation. Similar results have been obtained by others, Mészáros *et al*. (2004) with different woods, Ulloa *et al*. (2009) with sub-bituminous char and Australian bituminous char, Senneca (2007) with wood chips (*Pinus radiata*), pine seed shells, and exhausted olive husk, Aguiar *et al*. (2008) with shell citric, and Grammelis *et al*. (2009) with wood based products, and Wang *et al*. (2015) with wood. The third stage reached 800 °C, where about 90% of the mass of the starting material had been lost. Decomposing lignin, cellulose, and residual char takes place with the rearrangement of the carbon atoms present in the structure of the original biomass, mainly from the structure of lignin. Higher volume loss of volatiles and other compounds present in the material used takes place in the second and third stages. The TGA and DTG curves show that, with increasing heating rate, the conversion achieved at higher temperatures indicated an effect of intraparticle heat transfer processes on the overall degradation process, as well as competitive reactions that are affected by increasing the heating rate (Seong and Oladiran 2009, with switchgrass; Syed *et al.* 2011, with oil shale; Ferdinand *et al.* 2009, with pine wood chips; Skodras *et al*. 2007, with animal derived by-products; Corbetta *et al*. 2014). This phenomenon was more evident in Biomass 2 and was caused by the greatest consumption in energy of the ash. The influence of ash has been demonstrated in this process type (Raveendran *et al.* 1995, with 13 types of biomass in the Bombay region; Giudicianni *et al.* 2014, with *Arundo donax*). The most distinct points in the DTG curves are related to the values of temperature of the maximum thermal decomposition.

Figures 5 and 6 show an analysis of thermal decomposition for both samples over time. It can be observed that starting from 2 h, the normalized curve is parallel to the time axis which confirms the selection of 2 h for pyrolysis.

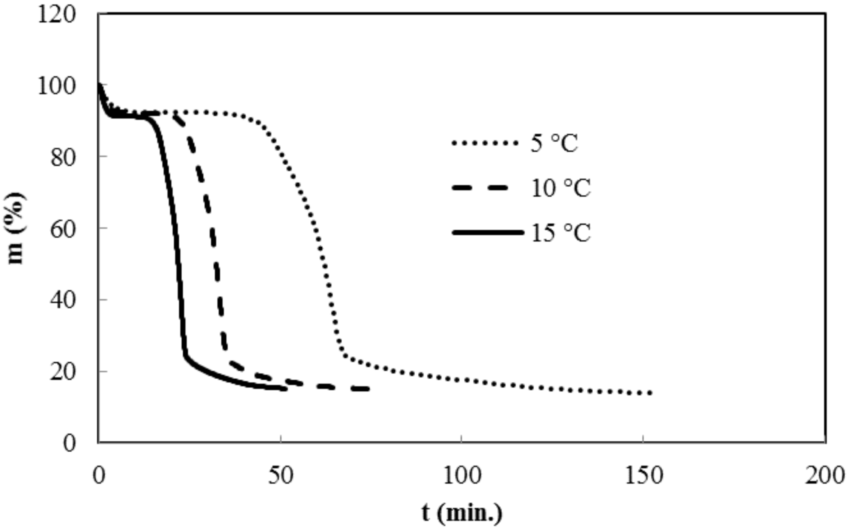

Fig. 5. Mass loss from thermal decomposition of Biomass 1 (wood without bark) at the heating rates of 5 to 15 °C/min

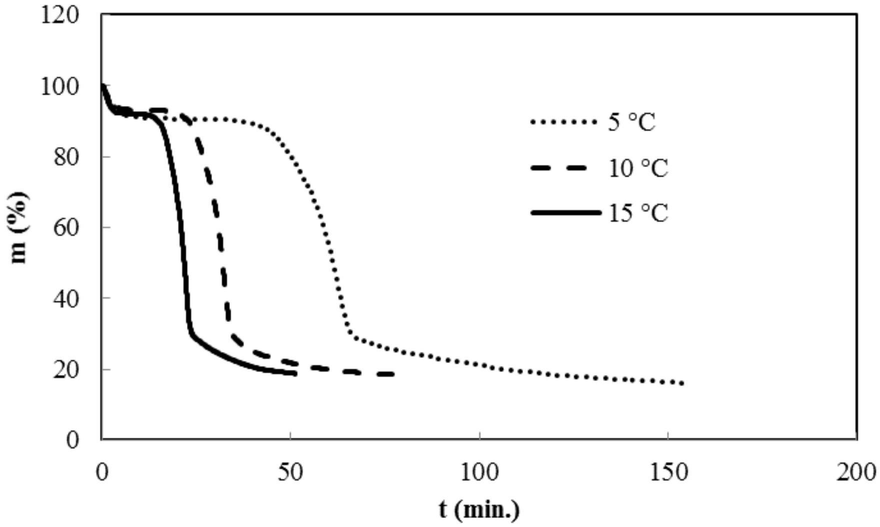

Fig. 6. Mass loss from thermal decomposition of Biomass 2 (wood with bark) at the heating rates of 5 to 15 °C/min

A first-order kinetic study was performed. Results by other authors have shown that the best values from the linear regression of the Arrhenius equation are obtained when the reaction order of the oxidative pyrolysis of the biomass is equal to 1 (n=1) (Aguado *et al.* 2002; Shen *et al.* 2009). The Ozawa–Flynn–Wall (Ceylan and Topcu 2014) method was used to determine the activation energy values plotted using the natural logarithms of the heating rates (ln B) against reciprocal temperature ($1/T$). To obtain the activation energy (E_a) in the different stages of thermal decomposition, the Arrhenius equation was applied. Seven different conversion values (α) are represented in different curves: 20%, 30%, 40%, 50%, 60%, 70%, and 80%. The ln B graphs versus $1/T$ are shown in Fig. 7 for Biomass 1 and Fig. 8 for Biomass 2.

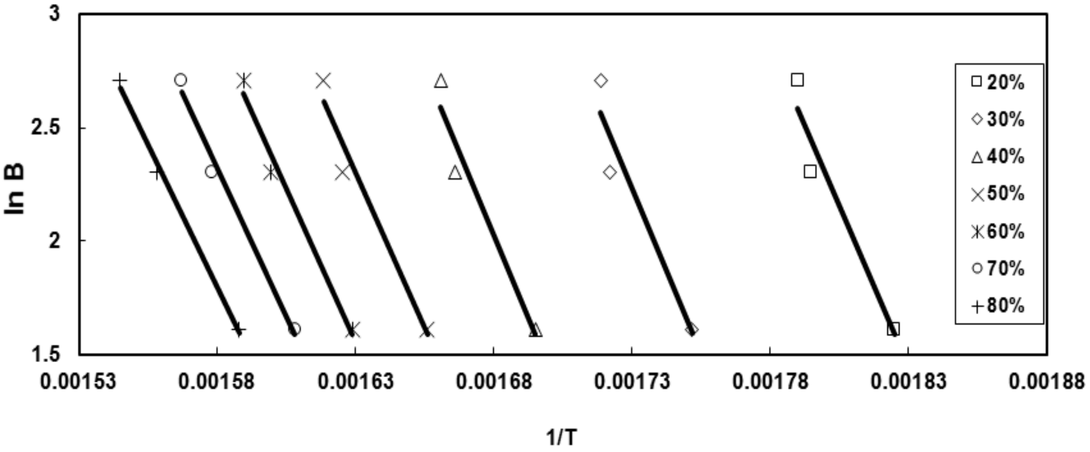

Fig. 7. Regression lines for conversion of 20 to 80% based on the Ozawa-Flynn-Wall method for Biomass 1 (wood without bark) at the heating rates of 5 to 15 °C/min

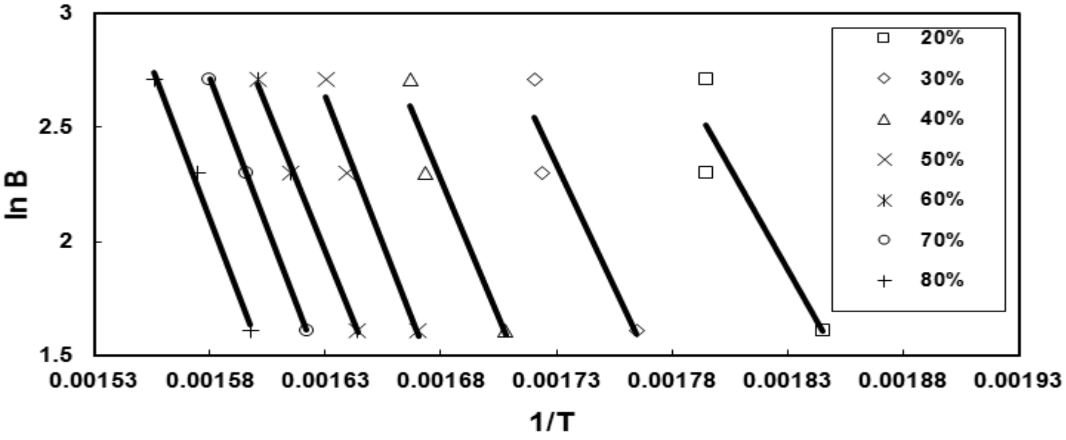

Fig. 8. Regression lines for conversion of 20 to 80% based on the Ozawa-Flynn-Wall method for Biomass 2 (with bark) at the heating rates of 5 to 15 °C/min

E_a values and temperature ranges are shown in Tables 2 and 3, respectively.

Table 2. Coefficient of Determination, Activation Energy at Different Conversion "*α*," and Heating Rate for Biomass 1 (wood without bark)

(*α*) (%)	E_a (kJ/mol) (K)	R^2	Temperature range (V 5-15 °C/min)
0.2	236.60	0.9418	275-286
0.3	243.15	0.9238	298-309
0.4	244.06	0.9474	317-329
0.5	227.28	0.9619	331-345
0.6	223.54	0.9838	341-356
0.7	216.41	0.9878	349-365
0.8	208.96	0.9946	356-374

Table 3. Coefficient of Determination, Activation Energy at Different Conversion "*α*," and Heating Rate for Biomass 2 (wood with bark)

(*α*) (%)	E_a (kJ/mol) (K)	R^2	Temperatura range (V 5-15 °C/min)
0.2	148.09	0.8706	269-284
0.3	179.45	0.908	293-308
0.4	203.15	0.9493	312-327
0.5	216.73	0.9746	326-340
0.6	209.29	0.9984	335-352
0.7	217.24	0.9999	343-360
0.8	221.57	0.9918	353-370

It can be observed that the values of E_a were not very high, which can be related to the youth of the selected trees. Juvenile wood in the tree is less complex in its structure of cellulose relative to the degree of polymerization and crystallinity. The lignin is less crosslinked, indicating a lesser degree of polymerization of the monomer units and a lower presence of aromatic systems (Orea *et al*. 2004, with eucalyptus wood). The lignin and the thermic cellulose are more easily removed when not at full maturity. Therefore the chemical reactions do not require higher E_a values. More homogeneity was observed in the values of Biomass 1 than in the values of Biomass 2, suggesting a diffusional control of the thermal decomposition process in Biomass 1 and not in Biomass 2. This decomposition behavior in Biomass 2 is due to the presence of a larger percentage of ash, which alters the process.

Upon completion of the thermal decomposition (80%), an increase in E_a was observed for the two biomasses. This process can be influenced by the possible formation of slag that occurs at elevated temperatures. Similarly, it is observed that the values of E_a for Biomass 2 were lower than those of Biomass 1, suggesting that catalytic activity of ash occurred in greater proportion than it did in Biomass 1, allowing chemical reactions to occur faster and with lower activation energy. The average E_a values of 233.37 kJ/mol for Biomass 1 and 199.36 kJ/mol for Biomass 2 confirm the above analysis. Similar values were obtained by other authors (Aguado *et al.* 2002, with polyethylene and polypropylene pyrolysis; Grammelis *et al*. 2009, with wood based products such as magazine paper, cardboard, recycling paper, newspaper, and copy paper; García *et al*. 2010, with *Leucaena leucocephala* and two composts with different maturation levels; Syed *et al.* 2011, with oil shale samples; Kim *et al.* 2014, with wood pine).

The values of E_a previously mentioned were used for the calculation of the factor frequency. Table 4 shows that there is an increased frequency of collisions of the particles during the process with increasing heating rate, with similar values for both biomasses. These values are in the range of those reported by many authors for n=1 according to Aguado *et al.* (2002). However, the lower value of E_a in Biomass 2 suggests that chemical collisions of the particles in Biomass 2 are more effective in the facilitation of the reaction than the collisions in Biomass 1.

Table 4. Frequency Factor (Z-s^{-1}) at Different Heating Rate

Heating rate (°C/min)	5	10	15
Biomass 1	$2.87{*}10^{8}$	$5.75\ {*}10^{8}$	$8.63{*}10^{8}$
Biomass 2	$9.60{*}10^{6}$	$1.92{*}10^{7}$	$2.88{*}10^{7}$

Pyrolysis Furnace

TGA followed the yield of char and decreased with increasing temperature. These char decreases were more pronounced from 250 to 380 °C, since the temperature increased the incidence of favorable biomass decomposition reactions; more volatile components arose from this and only remained in the fixed carbon residue form of carbon. Similar results of char yield versus temperature are reported in the literature (Ayllón *et al*. 2006 with borne; Strezov *et al.* 2007, with wood sawdust, bagasse, and macadamia nut shell; Apaydin *et al.* 2007, with pistachio shell; Özbay *et al.* 2008, with bio-oil obtained from fruit pulp). Also, the thermogravimetric study showed that after 2 h, the standard curve was completely parallel to the X axis.

From the above results, it was decided to control carbonization temperature and heating rate with a residence time of about 2 h. The samples were heated in the oven according to previous experimental methods using wood (Márquez *et al.* 2001, with *Pinus* and *Eucalyptus* wood) and according to TGA results. Char was obtained with a high percentage of fixed carbon and a necessary percentage of volatile compounds, ensuring good calorific values and good char power. Proximate analysis, elemental analysis, and the calorific value of carbons obtained are shown in Table 5.

Table 5. Characteristics of the Obtained Carbons (% db)

	AW40010	AW45010	AW50010	AWB45010
Proximate analysis (% mf)				
Ash (%)	1.64	1.75	2.45	3.61
Volatiles (%)	34.17	27.12	21.61	23.98
Fixed Carbon (%)	64.19	71.13	75.94	74.09
Elemental analysis (% mf)				
Carbon (%)	70.58	73.53	77.87	76.15
Hydrogen (%)	2.86	3.04	2.57	3.15
Nitrogen (%)	0.70	0.93	1.15	0.89
Oxygen** (%)	25.86	22.5	18.41	19.81
HHV(kJ/kg)	23 731.6	25 493	26 908	26 942
Carbon yield (% mf)	27.4	25.4	18.1	23

** Oxygen is determined by difference

The degree of carbonization increases with temperature, obtaining a solid with more high fixed carbon content, and less volatile higher calorific (Márquez *et al*. 2001). The higher heating value was obtained at the temperature of 400 °C, where coal retains as many volatiles. There was a correlation of calorific values with the values of the chemical composition, proximate analysis, and elemental analysis. These results are in the order of those reported in the literature (Márquez *et al*. 2001, with *Pinus* and *Eucalyptus* wood; Mesa *et al.* 2005, with elephant grass and sugar cane bagasse; Telmo and Lousada 2011, with wood tropical residues; Yin 2011, with agricultural by-products and wood; Skreiberg *et al.* 2011 with wood, demolition wood, coffee waste, and glossy paper).

Gases and Liquids

In Table 6 are shown the values of yields of gases, liquids, water, and char.

Table 6. Gas, Liquids, Water, and Char Yields Obtained

	Biomass 1 Wood without bark	Biomass 2 Wood with bark
Gases (%)	23,18	26,09
Liquids (%)	25,45	24,31
Water (%)	32,35	32,07
Char (%)	18,91	17,43

In Table 6, the highest percentage of gas was observed in the case of wood with bark. This is attributed to the catalytic action of the ash present. The biomass decays by breaking of the bonds within the structure. The result of this breaking is the formation of a large number of radical components of which part is volatile under the experimental conditions (Demirbas 2001a).

Table 7 shows the percentages of the products of pyrolysis gases under the conditions studied for slow pyrolysis. A higher percentage of CO over CO_2 was observed, which might favor the caloric value of the gas and biomass studied. A higher heating value of the gases was observed in the shell biomass, due to the catalytic activity of the ash, which increased the percentage of gases, mainly carbon monoxide. However, the high percentage of N_2 present greatly affected this value. Even under the conditions studied, the fundamental products obtained were not gases; similar results for lignocellulosic materials were obtained in other studies (Demirbas 2001b, with cotton cocoon shell, tea factory waste, and olive husk; Ferdinand *et al.* 2009, with maritime pine wood chips, and Aguiar *et al.* 2013, with solid residue the orange industrial process, gasification).

Table 7. Product Gas Composition

	Biomass 1 Wood without bark	Biomass 2 Wood with bark
Hydrogen (%)	2.81	0.55
Oxygen (%)	7.45	3.26
Nitrogen (%)	59.20	56.03
Methane (%)	3.92	3.77
Carbon monoxide (%)	17.01	27.25
Carbon dioxide (%)	9.61	9.12
LCV (kJ/m^3)	3858,7	4859,4

Figures 9 and 10, show the percentage of condensable for Biomass 1 and Biomass 2, respectively. It can be observed that the percentage of aromatics was much higher in Biomass 1 because aromatics are extractable compounds with greater presence in the bark. The difference in the percentage of aromatic hydrocarbons and oxygenated compounds in both samples of biomass, could be the result of the catalytic action of the Biomass 2 ash, causing catalytic cracking (Shen *et al*. 2009, with aspens, birch, oak and pine). There have been similar results reported in the literature (Beis *et al*. 2002 with safflower seeds (*Carthamus tinctorius* L.); Demirbas 2006, with nut shells; Apaydin *et al*. 2007, with pistachio shells; Özbay *et al*. 2008, with bio-oil obtained from fruit pulp, Aguiar *et al.* 2008, with orange peel residues and particle size of 0.800 mm). Figures 11 and 12 show the chromatograms (CC/MS) for Biomass 1 and Biomass 2, respectively.

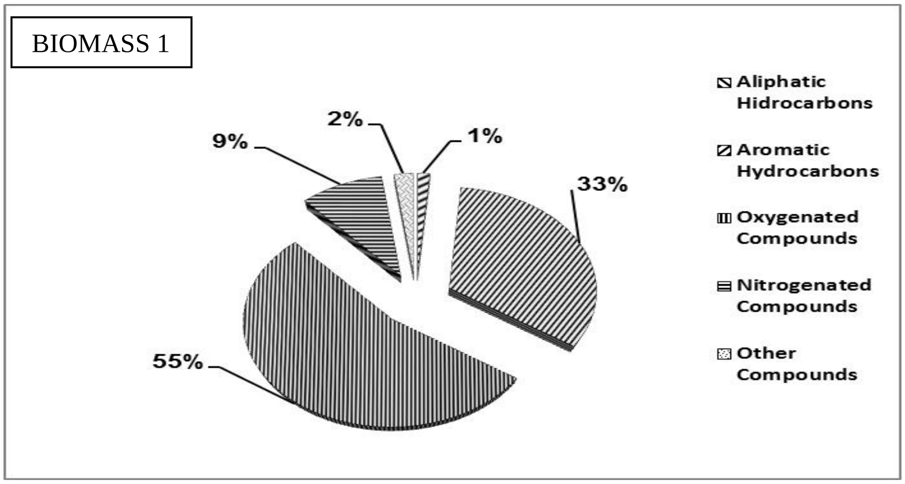

Fig. 9. Composition of the liquid fraction produced in pyrolysis, Biomass 1.

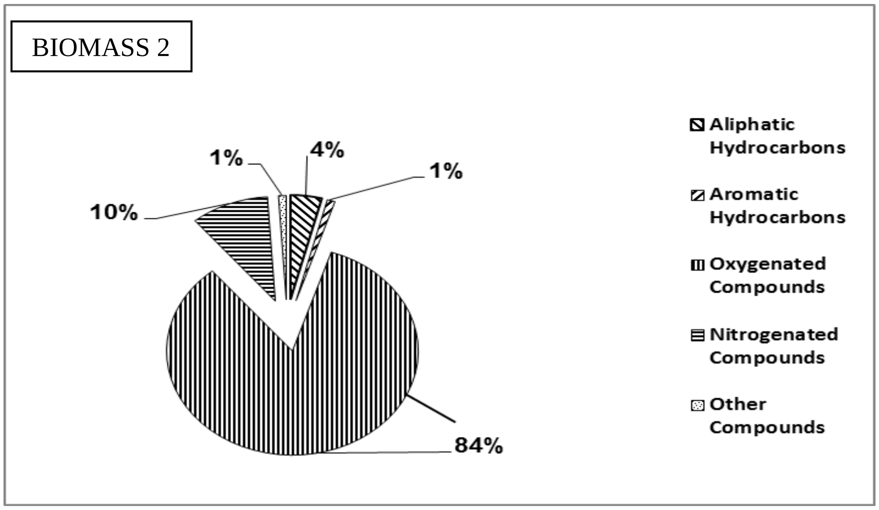

Fig. 10. Composition of the liquid fraction produced in pyrolysis, Biomass 2.

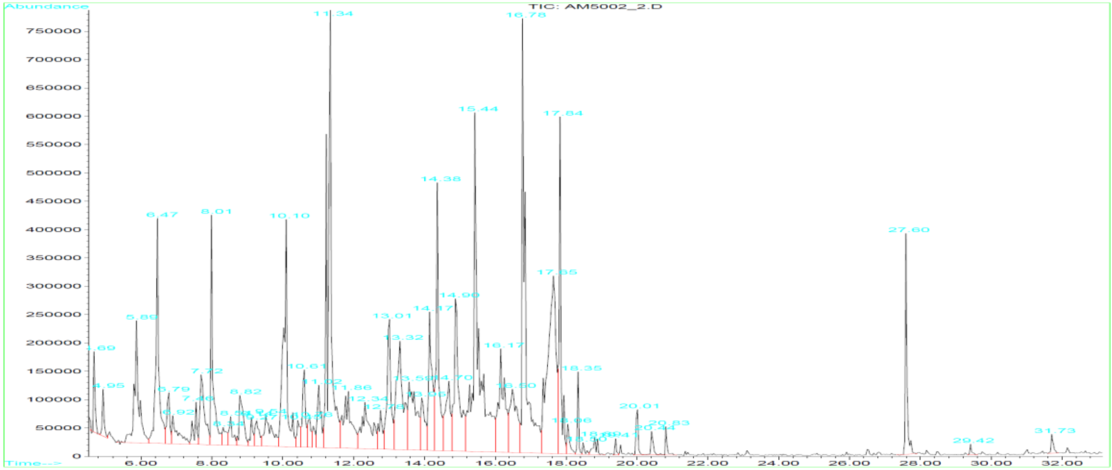

Fig. 11. GC/MS for Biomass 1

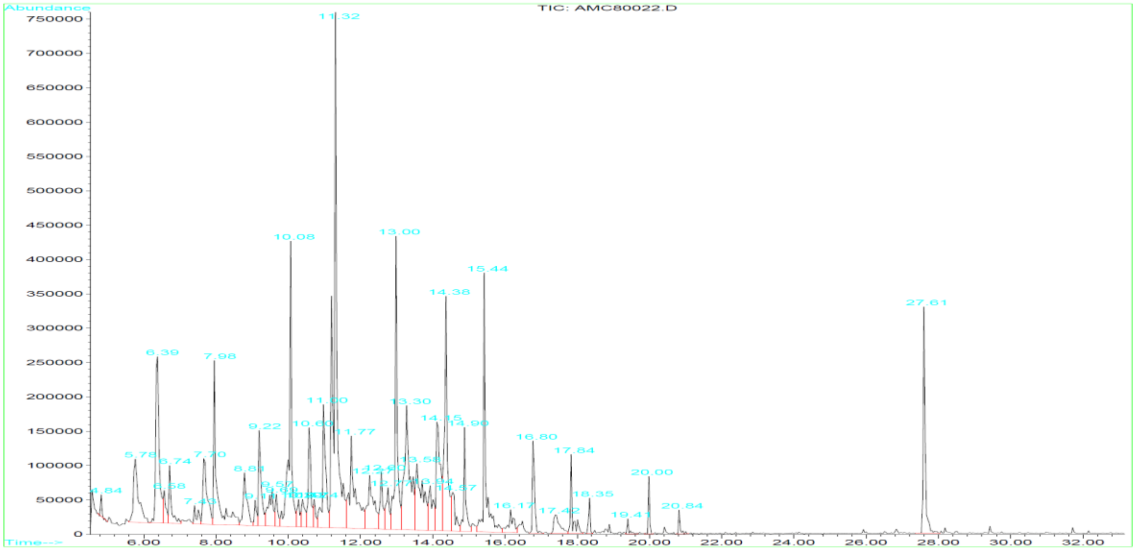

Fig. 12. GC/MS for Biomass 2

CONCLUSIONS

1. Devolatilization maximum values between 250 °C ± 20 and 380 ± 20 °C were observed; from the second hour, the normalized curve was parallel to the time axis, which confirms the selection of 2 h for pyrolysis.
2. The structures of the timber cell wall chemical components, including cellulose and lignin, were not structurally complex in the way they met and interacted in the wood. This was demonstrated by the E_a values from the different stages of thermal decomposition of 228.57 kJ/mol for Biomass 1 and 199.36 kJ/mol for Biomass 2.
3. The values of coefficient of determination (R^2) from 0.9418 to 0.9946 for wood bark and from 0.8706 to 0.9918 wood with bark, indicate the reliability of the first-order reaction model.
4. The caloric values obtained were: Biomass 1 (16962 kJ/kg), Biomass 2 (16974 kJ/kg), chars from Biomass 1 (between 23731 y 26 942 kJ/kg) and gas from Biomass 1 and Biomass 2 (3858.7 and 4859.4 kJ/m^3, respectively).

ACKNOWLEDGMENTS

The authors are grateful for the support of CAPES-MES (CGCI nº 002/2009) Brazil-Cuba for financing the activities that led to these results, the University of Campinas (SP-Brazil), and the University of Pinar del Rio (UPR, Cuba).

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Article submitted: October 23, 2014; Peer review completed: January 7, 2015; Revised version received and accepted: January 18, 2015; Published: January 30, 2015.