Chemical Composition and Thermal Properties of Tropical Wood from the Yucatán Dry Forests

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Six different species of dry forest trees were collected, and their chemical compositions and thermal properties were determined. Three of the six species (*Senegalia gaumeri, Havardia albicans*, and *Lysiloma latisiliquum*) were chosen due to their high preference as firewood in local communities, while the remaining three species (*Croton glabellus, Lonchocarpus yucatanensis,* and *Neomillspaughia emarginata*) were chosen because of their abundance at the sampling site. The chemical compositions were consistent with the composition of tropical woods reported in previous literature, with an ash content of 4.8% to 6.8% and total extractible content in the range of 15.4% to 28.5%. The lignin content was in the range of 17.6% to 24.0%, while the range of holocellulose was 53.9% to 63.0%. The calculation of the calorific values was performed using the elemental analyses, and values ranging between 16.2 and 18.5 MJ/kg were obtained. The fuel value index (FVI) values for the samples indicated that *S. gaumeri* and *L. yucatanensis* were the best species for fuelwood given their high densities and relatively high calorific values. The kinetics of pyrolysis showed a higher level of reactivity for *H. albicans* and *L. yucatanensis* compared to the other species studied.

Keywords: Firewood; Chemical composition; Thermal analysis; Elemental analysis; Kinetic analysis; Dry forests

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INTRODUCTION

Traditional biomass, mostly in the form of fuelwood (firewood and charcoal), remains an important energy source, especially in the rural regions of developing nations. In 2015, approximately half of all extracted wood in the world was used as fuelwood, representing 1,866 million cubic meters (FAO 2018). The sustainability of this energy source has evolved from the forecasting of generalized depletion of forests in the 1970s to a less dire view in recent years. This view includes recognizing complex patterns of supply and substitution of demand that have cushioned the expected depletion of woody biomass in many regions (Arnold *et al.* 2006). New analyses and tools have recently been used to ascertain the sustainability of fuelwood as an energy source in terms of detailed geographic analysis (Ghilardi *et al.* 2016) and for greenhouse gas (GHG) emissions (Bailis *et al.* 2015).

The traditional and current main way to obtain energy from firewood for cooking, water heating, and space heating, has been combustion; however, these uses of firewood, especially in open (or three stone) fires, is concerning due to their negative health impact (Naeher *et al.* 2007; Valerio 2012). They are also considered highly inefficient (Hoffmann *et al.* 2015) and reveal a type of energy poverty that should be reduced (Pachauri and Spreng 2011). The gradual replacement of firewood in traditional uses can occur as fuel switching or through an overlap of different energy sources, including fuelwood (the concept of fuel stacking), which helps households to climb the energy ladder (Heltberg 2004; Van der Kroon *et al.* 2013) to more convenient forms of energy sources. For example, the development of improved fuelwood cookstoves (ICS) is a technological solution that aims to reduce the consumption of firewood (thus improving sustainability) and exposure to harmful smoke (Ruiz-Mercado and Masera 2015). Other thermochemical processes to produce bioenergy from fuelwood are gasification, which produces a gas that can be combusted for heat or used as the fuel of an internal combustion engine, and pyrolysis, which produces charcoal and liquids for heat and transportation fuels, respectively (Panwar *et al.* 2012; Kan *et al.* 2016; Tag *et al.* 2016; Ezhumalai and Kumar 2017). Several factors affect the performance of the products generated in the previously mentioned thermochemical processes, mainly the biomass chemical composition (Ezhumalai and Kumar 2017), type, and pretreatments (physical, chemical, or biological) (Kan *et al.* 2016; Tag *et al.* 2016). There have been few studies on the chemical composition of the woody biomass traditionally used as fuelwood in the rural areas of developing countries. Fuelwood is considered to have a higher chemical quality if it contains a higher extractive content and lower ash and holocellulose contents, resulting in a higher calorific value (Kataki and Konwer 2001). Better fuelwood is also consistent with a higher density, as the physical quality permits a higher carrying energy capacity, as shown in studies in Africa (Abbot and Lowored 1999), India (Kataki and Konwer 2002), and South America (Cardoso *et al.* 2015; Díez and Pérez 2017). Additionally, the kinetic study of woody biomass volatilization also gives valuable insight on its suitability as a source of energy and the design parameters for pyrolysis and gasification. The basic parameters of the kinetic behavior of the materials are the activation energy (E_a), pre-exponential factor or frequency factor (A), and kinetic constant (k) (White *et al.* 2011).

In México, firewood remains an important source of bioenergy, and it is the most important energy resource in the rural areas in the state of Yucatán. However, the calorific power of fuelwood is used in an inefficient way in three stone cooking fires or traditional ovens, with an efficiency of approximately 5% (De los Ríos 2010). In a recent survey covering six communities in the northeastern part of the state, it was found that the average consumption of firewood was 2.06 kg per day per person. The firewood is extracted from nearby vegetation, traditional planting areas, and patios, and it was found to require trips averaging 3.8 km (Quiroz-Carranza and Orellana 2010). The latest available inventory found a total of 166 million cubic meters of woody biomass in the standing woods in the state of Yucatán (SEMARNAT 2014). The vegetation types present in the state of Yucatán can be described as semi-evergreen medium-statured forest, semi-evergreen low-statured forest, semi-deciduous medium-statured forest, and deciduous low- or medium-statured forest, with all of them being subtypes of dry tropical forests (less than 2000 mm/year of rain) (Urquiza-Haas *et al.* 2007). Dry tropical forests are present in Asia, Africa, and Latin America, and their main role in the demand for energy is the provision of fuel in the forms of wood and charcoal (Blackie *et al.* 2014). The exploitation of fuelwood in the state of Yucatán is heavily influenced by the presence of swidden agriculture (Daniels *et al.* 2008; Hartter *et al.* 2008) and the retreat of sisal plantations in recent decades (González-Iturbide *et al.* 2002). On the other hand, there are very few works on the composition and thermal properties of most species of the dry forest of Mexico.

This work aims to determine the chemical composition and thermal properties of wood biomass available in the Yucatán state and their suitability for bioenergy production.

The six species studied were chosen due to their preference as firewood by the local rural population or their abundance.

EXPERIMENTAL

Materials

Study site

The state of Yucatán is in the southeastern part of the country, occupying the northernmost portion of the Yucatán Peninsula between the latitudes 21° 38' 20" N to the north and 19° 33' 00" N to the south and between the longitudes 87° 31' 55" W to the east and 90° 24' 25" W to the west. The site for the sampling of material is a tract of land located in the northwestern part of the state located between latitudes 21° 08' 19" N and 21° 07' 37" N and between longitudes 89° 46' 29" W and 89° 47' 12" W. This area is endowed with forests that have suffered relatively low disturbance in recent years.

Sampled species

Six different species of tropical trees were collected from the study site. These species were chosen as a representative of the vegetation predominant in the state of Yucatán and are listed in Table 1. The first three species listed were chosen due to the highest preference (measured as the relative frequency of use) for them as sources of firewood due to their easy ignition, fire sustenance, and low emissions of smoke, as indicated in a survey of fuelwood use and species preference in communities in the region (Quiroz-Carranza and Orellana 2010). The remaining three species were chosen due to their high prevalence in the plot of land sampled (measured as the importance value, from an unpublished survey, Sigfredo Edmundo Escalante Rebolledo, personal communication). At least three trees of similar size of each species listed in Table 1 were selected at the study site, and one young branch, approximately a meter long and 7 cm in diameter, was taken in May 2015 from each tree.

Table 1. Species Collected in a Tropical Forest Land Area Located in the Northwestern Part of the State of Yucatán in México and Evaluated in this Work

Sample	Scientific Name	Mayan Name	Family	Relative Frequency of Use	Importance Value
1	*Senegalia gaumeri*	Boxkatsim	Fabaceae	26.82	N.d.
2	*Havardia albicans*	Chukum	Fabaceae	18.27	N.d.
3	*Lysiloma latisiliquum*	Tsalam	Fabaceae	16.88	N.d.
4	*Croton glabellus*	P´eresk´uch	Euphorbiaceae	N.d.	0.4594
5	*Lonchocarpus yucatanensis*	Ya´ax xu´ul	Fabaceae	N.d.	0.2703
6	*Neomillspaughia emarginata*	Sakits'a	Polygonaceae	N.d.	0.2698

Methods

Analysis of samples

The branches sampled were dried at room temperature (average temperature of 26 °C) for approximately four months prior to analysis. The branches with bark were cut into small pieces and ground to a reduced size. The ground material was sieved, and the fraction retained between 40- and 60-mesh (420 to 250 microns) was used in the chemical, elemental, and thermal analyses. Unless otherwise indicated, the determinations were carried out by duplicate.

Determination of the moisture content and ash

The moisture content was determined following the ASTM E871-82 (2013) method and was carried out in triplicate. Approximately 2 g of material was weighed in ceramic crucibles previously placed at constant weights. The crucibles were placed in a convection oven at 100 °C until a constant weight was achieved. The moisture percentage was calculated by the relation between the lost weight and wet sample weight.

The ash content was determined following the ASTM D1102-84 (2013) method. The dried samples were placed in a muffle furnace and heated to 600 °C until a constant weight was obtained. The percentage of ash was calculated by the relation between the residual weight and the dry sample.

Chemical composition

The material was dried in a convection oven to determine the moisture content. The dried material was analyzed for the determination of the extractives in the solvents, water, and Klason lignin. The extractives were determined using the TAPPI T204 cm-97 (2007) method. The sieved material was placed in a Soxhlet apparatus in an extraction cartridge made with filter paper at a constant weight. The extraction was made with a benzene/ethanol mixture (2:1) for a minimum of 5 h or 16 extraction cycles, and then, the cartridges were drained and dried to a constant weight in a convection oven. The process was repeated with 95% ethanol as the dissolvent. The water extraction was performed using the TAPPI T207 cm-99 (1999) method. The material resulting from the solvent extraction was placed in 900 mL of distilled water in an Erlenmeyer flask and was heated to a boil for an hour. The resulting suspension was filtered with a Buchner filter. The boiling process was repeated two more times, and the resulting solid was dried to a constant weight in a convection oven. The relationship between the weight loss in each extraction and the dry weight represents the percentage of extractives at each stage.

The Klason lignin was determined according to the TAPPI T222 (2011) modified technique. During the analysis, 1 g of material free of extractives was subjected to acid hydrolysis with 15 mL of 72% (w/w) H_2SO_4. Using a water bath, the sample was kept at a constant temperature of 15 °C while being agitated for 2 h. Then, the suspension was diluted with water to an approximate concentration of 4% and kept boiling for 4 h. The solution was then filtered using an F-type glass filter previously put to a constant weight, with the insoluble material dried in a convection oven. The lignin content was determined using the following equation,

$$\%\,Lignin = \left[\left(\frac{m_\mathrm{f}}{m_\mathrm{i}}\right) * \left(1 - \frac{Ext_\mathrm{tot}}{100}\right)\right] * 100 \tag{1}$$

where m_f is the weight recovered (g), m_i is the weight of sample-free extractives (g), and Ext_tot is the percentage of total extractives (%).

The content of holocellulose (cellulose + hemicellulose) was determined as the difference at 100% with respect to the content of lignin and extractible.

Elemental analysis and the higher heat value (HHV)

An elemental analysis of the wood samples was performed. This analysis is also called CHONS, considering that for practical purposes, almost all organic matter is composed of the elements carbon, hydrogen, oxygen, nitrogen, and sulfur. For this test, a Thermo Scientific FLASH 2000 Elemental Analyzer (Thermo Scientific, Rodano, Milan, Italy) was used. Between 2 to 3 g of each tree species material was introduced in tin capsules, as required for the technique, to be automatically sampled and analyzed. The values obtained in the elemental analysis of wood were used to determine the calorific value of each tree sample using the Francis and Lloyd formula (Francis and Lloyd 1983). The formula, expressed as the higher heating value, is shown below,

$$HHV\ (\text{kJ/kg}) = 357.8\text{C} + 1135.6\text{H} + 54.9\text{N} + 119.5\text{S} - 85.4\text{O} - 974 \tag{2}$$

where C, H, N, S, and O are the percentages (%) of carbon, hydrogen, nitrogen, sulfur, and oxygen in the sample, respectively.

Density and fuel value index (FVI)

Cylindrical sections (5 cm in diameter and 15 cm in length) of each dry species were obtained; the dimensions were measured carefully, and the specimens were weighed to determine density. These results, together with the results from the calorific value, as well as moisture and ash contents, were used to obtain the FVI using the formula below (Rai *et al.* 2002). In this case, the moisture content is the equilibrium moisture after drying of the samples.

$$FVI = \frac{\text{Calorific value}\left(\frac{\text{kJ}}{\text{g}}\right) \text{ x Density } (\frac{\text{g}}{\text{cm}^3})}{\text{Ash content}\left(\frac{\text{g}}{\text{g}}\right) \text{ x Moisture content } (\frac{\text{g}}{\text{g}})} \tag{3}$$

Statistical analysis

Analysis of varianza (ANOVA) was performed to determine the statistical differences between the chemical composition, the elemental components of the wood among the six species and the calorific value and FVI value. The results were analyzed using Minitab Statistical Software. Tukey test ($p<0.05$) was performed for comparison of averages.

Thermal and kinetic analysis

To investigate the thermal and kinetic properties of the samples, thermogravimetric analysis (TGA) tests were run using several heating rates (2, 5, 10, and 15 K/min). A TGA Q8000 Perkin Elmer thermogravimetric balance (Waltham, MA, USA) was used to run heating ramps from 310 to 980 K with a constant 20 mL/min flow of nitrogen. A model-free equation based on the Arrhenius expression was used to determine the activation energy (Ea, kJ/mol) and the frequency factor (A, 1/min), also called the pre-exponential factor. Using the model free equations, it was possible to obtain the kinetic parameters of a solid-state reaction without knowing the reaction mechanism. The model-free Kissinger method (Slopiecka *et al.* 2012) allows for the determination of the value of the activation energy from a plot of ln (β/T_m^2) against $1000/T_m$ for a series of heating rates (β) in K/min, where T_m is the temperature (K) peak of the DTG curve and R is the gas constant (8.314 J/mol K). The equation used is as follows:

$$ln\left(\frac{\beta}{T_m^2}\right) = ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m} \quad (4)$$

RESULTS AND DISCUSSION

Statistical Analysis

The results of the analysis of variance (ANOVA) showed that in all cases there is statistical significance ($p < 0.05$) between the different types of species with respect to the chemical composition (Table 2) as well as with the values of HHV and FVI (Table 3). However, the multiple range analysis (Tukey test) showed that not all the means were significantly different.

Firewood Chemical Characterization

The results of the chemical characterization of the firewood samples are shown in Table 2. Benzene/ethanol extractives ranged from 4.7% (*L. latisiliquum*) to 10.3% (*L. yucatanensis*), ethanol extractives ranged from 0.8% (*L. yucatanensis*) to 5.1% (*S. gaumeri*), and water extractives ranged from 7.1% (*H. albicans*) to 14.3% (*L. latisiliquum*). The benzene/ethanol mixture and ethanol extract compounds had low and medium polarity, respectively, due to waxes, fats, resins, and a portion of wood gums. Water extraction removes tannins, gums, sugars, starches, and color producing chemicals (Basu 2013). In general, these compounds are responsible for the color and odor of the plant and are metabolite intermediates of structural compounds. These are sources of stored energy and provide resilience to microbial attacks on plants. The total extractable content obtained in this work was consistent with the results reported in literature for tropical species with values up to 20% (Pettersen 1984; Balogun *et al.* 2014). The total extractable contents ranged from 16.6% for *H. albicans* to 27.9% for *S. gaumeri*. The lignin values obtained from the studied species ranged from 17.6% for *S. gaumeri* to 24.0% for *N. emarginata*. These values are lower than those reported for other tropical species, such as *Acacia* species and *Albizia pedicellaris*, which have lignin contents of up to 30% (Nasser and Aref 2014; Balogun *et al.* 2014). This may be due to the use of young branches that are less lignified compared to the older branches or the trunk of the trees. These results were consistent with the high contents of extractables obtained in the samples with lower lignin contents. The content of holocellulose varied from 54% to 63%, with the samples preferred as firewood being those that presented the lowest holocellulose values. Elevated extractive and lignin contents in woody biomass are positively correlated with the energy content (Demirbas 2009; Moya and Tenorio 2013), which could prove positive for the use of these materials as firewood.

Elemental Analysis, Heating Values, and Fuel Index Values

Table 3 shows the elemental analysis for the wood samples collected, as well as the calculated calorific values using these results. The table also shows the calculated FVI using the density, ash, and humidity values.

Table 2. Chemical Compositions of the Firewood Species

Species	Extractable (%)			Extractable Total (%)	Lignin Klason* (%)	Holocellulose** (%)
	Benzene-ethanol	Ethanol	Water			
S. gaumeri	8.65^{b} (0.16)	5.13^{a} (0.17)	14.12^{a} (0.95)	27.90^{a} (1.28)	17.64	54.46
H. albicans	5.54^{c,d} (0.62)	4.00^{a,b,c} (0.87)	7.10^{c} (0.16)	16.65^{d} (0.09)	21.57	61.88
L. latisiliquum	4.74^{d} (0.01)	4.90^{a,b} (0.19)	14.33^{a} (0.17)	23.96^{b} (0.16)	19.89	56.15
C. glabellus	6.63^{c} (0.28)	2.35^{c,d} (0.60)	9.21^{b} (0.05)	18.19^{c,d} (0.28)	20.59	61.22
L. yucatanensis	10.29^{a} (0.04)	0.75^{d} (0.11)	8.72^{b,c} (0.71)	19.66^{c} (0.91)	19.37	62.84
N. emarginata	8.11^{b} (0.01)	3.05^{b,c} (0.35)	7.15^{c} (0.33)	18.30^{c,d} (0.20)	23.95	57.75

Value between parentheses ( ) correspond to standard deviation.
Values followed by different lower-case letters are significantly different.
* Average was corrected using the average value of total extractable.
** Holocellulose was calculated using the average value total extractables and lignin content.

It was observed that the species studied, being a lignocellulosic material with lignin, cellulose, and hemicellulose as greater components, was composed of carbon and oxygen as the major elements, with percentages of 42.7% to 48.8% and 46% to 51.6%, respectively. The percentage of hydrogen was lower, with values of approximately 5%; the presence of sulfur and nitrogen in the samples, with values lower than 0.06% and 0.08, respectively, was also determined. The calorific values for the wood samples calculated from the elemental analysis ranged from 16.2 and 18.4 MJ/kg, which was similar to the range of values reported in the literature for forest waste and branches (Garcia *et al.* 2014). For example, the calorific value of black poplar and orange tree branches was reported to be 18.4 MJ/kg and 16.3 MJ/kg, respectively. The highest content of carbon in *L. yucatanensis* resulted in a HHV of 18.45 MJ/kg, which was higher than the species preferred as firewood (*S. gaumeri*, *H. albicans*, and *L. latisiliquum*).

Although the HHV was an important parameter in the selection of plant species as firewood, there are other factors, such as the ability to produce ember, low humidity, ease of flammability, *etc.*, that must be considered for species selection. This is reflected in other characteristics of plants, such as the moisture content, density, and ash content. The FVI considers this characteristic and it can be used as a criterion to select the best species for use as firewood.

Table 3 shows that the species *S. gaumeri*, *H. albicans*, and *L. yucatanensis* had densities greater than 1 g/cm^3; *C. glabellus* and *N. emarginata* had densities of 0.88 and 0.85 g/cm^3, respectively, and *L. latisiliquum* had the lowest density of 0.59 g/cm^3. The highest values of densities obtained in this work, with respect to those reported in literature for tropical wood (densities < 1), occurred because in the literature the densities were calculated from the dry weight and the volume of green wood. In this work, the density was calculated from the dry weight with respect to the volume of the wood at the reported moisture content (8.3% to 9.8%).

Table 3. Elemental Analysis and Fuel Characterization of Firewood Samples

Species	Elements, Weight Percentage (%)					Calorific Values (kJ/kg)	Density (g/cm^3)	Moisture (%)	Ash (%)	FVI
	C	H	O	N	S					
S. gaumeri	44.65^{b} (0.01)	5.92^{a} (0.06)	49.35^{b} (0.06)	0.08	0.00	17514^{b} (55)	1.126^{a} (0.62)	8.32^{a} (0.52)	5.83^{b,c} (0.05)	4088^{a} (526)
H. albicans	42.66^{c} (0.14)	5.64^{a,b} (0.11)	51.63^{a} (0.25)	0.01	0.06	16293^{c} (193)	1.030^{a,b} (0.059)	9.84^{a} (0.12)	6.82^{a,b} (0.57)	2502^{a,b,c} (125)
L. latisiliquum	43.81^{b,c} (0.35)	5.61^{a,b} (0.07)	50.53^{a,b} (0.28)	0.00	0.05	16763^{b,c} (67)	0.591^{b} (0.023)	8.40^{a} (0.18)	4.77^{c} (0.42)	2474^{b,c} (179)
C. glabellus	44.81^{b} (0.09)	5.71^{a,b} (0.05)	49.44^{b} (0.14)	0.00	0.04	17326^{b} (101)	0.876^{b} (.086)	8.67^{a} (0.14)	5.30^{c} (0.26)	3316^{a,b,c,} (519)
L. yucatanensis	48.82^{a} (0.64)	5.18^{b} (0.14)	45.98^{c} (0.81)	0.00	0.02	18452^{a} (462)	1.006^{a,b} (0.030)	8.34^{a} (0.93)	5.87^{b,c} (0.58)	3826^{a,b} (593)
N. emarginata	43.61^{b,c} (0.28)	5.22^{b} (0.25)	51.11^{a} (0.04)	0.00	0.06	16200^{c} (177)	0.846^{b} (0.068)	8.72^{a} (0.13)	7.22^{a} (0.22)	2177^{c} (189)

Value between parentheses ( ) correspond to standard deviation.
Values followed by different lower-case letters are significantly different.

The ash content of the species varied in the range of 4.8% for *L. latisiliquum* to 6.8% for *H. albicans*. These ash values agreed with the values reported for tropical woods (Demirbas 2009). The moisture content was similar for all species, and in this case, was the moisture recovered from the wood after drying.

The FVI fell in a range between 2,177 and 4,088. These changes in the FVI were due the variations in the density, as well as ash and moisture contents of the species. A high density had a positive effect on the FVI, whereas high ash and moisture contents had a negative effect. Species with a high density are preferred because these species keep the embers for a longer period. It can be observed that the highest FVI was obtained by *S. gaumeri* (4,088), which had a high density (1.126 g/cm^3) and low ash content (5.8%). The lowest value FVI (2,177) was obtained by *N. emarginata*, which had a density of 0.846 g/cm^3 and ash content of 7.2%.

Thermal Analysis

Thermogravimetric analysis

Figure 1 shows thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA) curves of the firewood species obtained at a heating ramp of 10 °C. Three zones of weight loss were observed in the TGA curves. The first one (50 to 120 °C) was due to the loss of humidity (10%). The second was in the range of 220 to 380 °C, with a weight loss of 58% for *L. latisiliquum* and *N. emarginata* and 66% for the other species. In this zone, the decomposition of the compounds of low molecular weight occurred together with the decomposition of the hemicellulose and the start of the decomposition of the cellulose. For all samples, most of the biomass volatilization occurred before 400 °C. The last zone (400 to 700 °C) was attributed to the decomposition of cellulose and lignin with a mass loss of 12%. Due to this loss, the thermal decomposition was carried out under a nitrogen atmosphere, which was similar to the pyrolysis process, and the formation of a carbonaceous fraction (residual mass) of 12% to 24% at 700 °C was obtained. The lowest residual mass was 11.4% for *L. yucatanensis*, and the highest was 24.6% for *N. emarginata*. This behavior can be attributed to the last species having high ash and lignin contents. Ash is the inorganic material that remains after the volatilization of organic material, and it has been reported that species with a high lignin content produced more carbonous residue after pyrolysis. The DTGA thermogram (Fig. 1b) shows the drops in the mass of the TGA curves as peaks, where the maximum of the peak was where the maximum rate of decomposition of the samples was observed. These curves were very similar for the samples of firewood, with the maximum rate of volatilization ranging from 355.5 °C for *L. latisiliquum* to 365.4 °C for *S. gaumeri*.

Pyrolysis kinetic analysis (Kissinger method)

Figure 2 shows the TGA and DTGA for *S. gaumeri* carried out at four different heating rates (2, 5, 10, and 15 K/min). It was observed that the heating rate influenced the position of the TGA curves, and a displacement curve at higher temperatures was observed with an increase in the heating rate. This is best seen in the DTGA curves, where a shift of the maximum decomposition temperature (TDmax) to higher values can be seen with an increased heating rate.

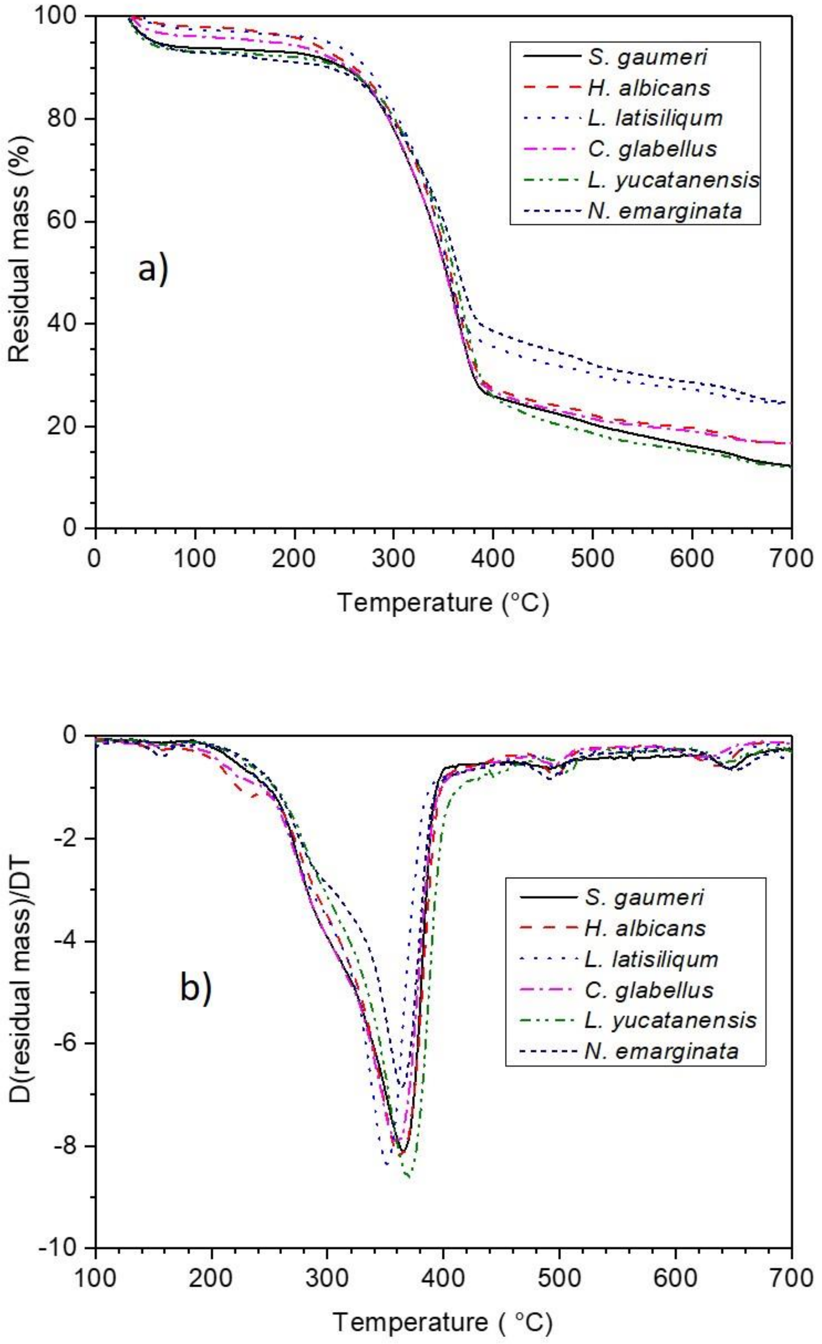

Fig. 1. (a) TGA and (b) DTGA thermograms of the firewood species

The TDmax and heating rate were used to determine the values of the activation energy (E_a) and the frequency factor (A) of the pyrolysis process using the Kissinger method. In this method, a plot of $\ln(\beta/T_m^2)$ against $1000/T_m$ (Fig. 3) resulted in a straight line, and the values of E_a and A can be obtained according to Eq. 4 from the slope and intercept with respect to the y-axis, respectively.

The results of the Kissinger analysis for all species are summarized in Table 4. It can be observed that the activation energies from the firewood were in the range of 138 to

233 kJ/mol, while the frequency factor was in the range of 6.62 x 10^7 to 6.34 x 10^{15} min^{-1}. These values were in accordance with the values obtained with the same or different methods for other species. For poplar, values of 154 kJ/mol for the activation energy and 2.14 x 10^{12} for the frequency factor have been reported (Slopiecka *et al.* 2012). For tropical trees, such as teak (*Tectona grandis*) and obobo (*Guarea thompsonii*), values of the activation energy of 137 and 149 kJ/mol and frequency factor values of 3.20 x 10^{12} and 6.37 x 10^{16}, respectively, were found using a model-fitting method of a third order reaction (Oluoti *et al.* 2014). The activation energies and frequency factor values can potentially be used for biomass gasification modeling. For example, using downdraft gasification models that combine transport and kinetic modeling (Patra and Sheth 2015).

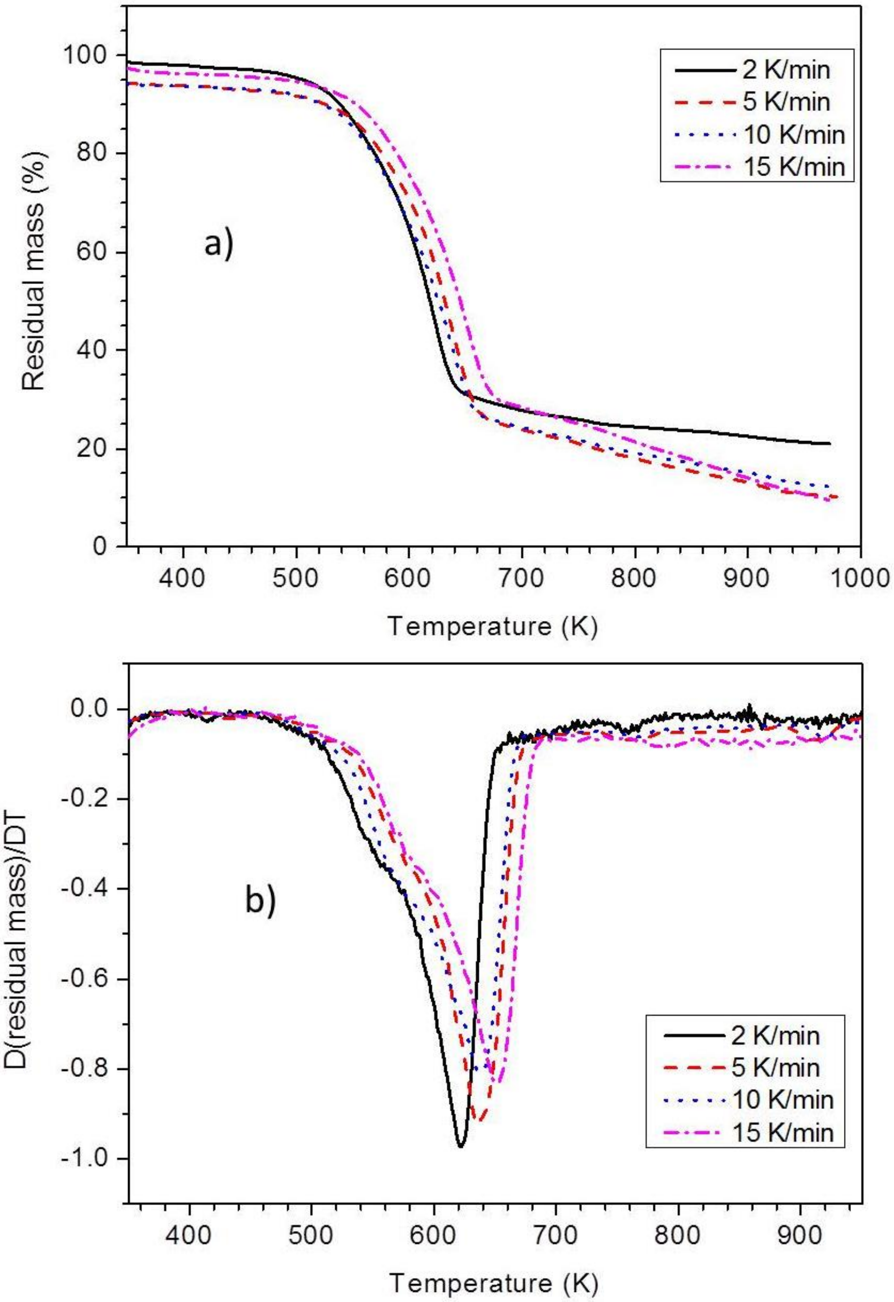

Fig. 2. (a) TGA and (b) DTGA curves of *S. gaumeri* at different heating rates

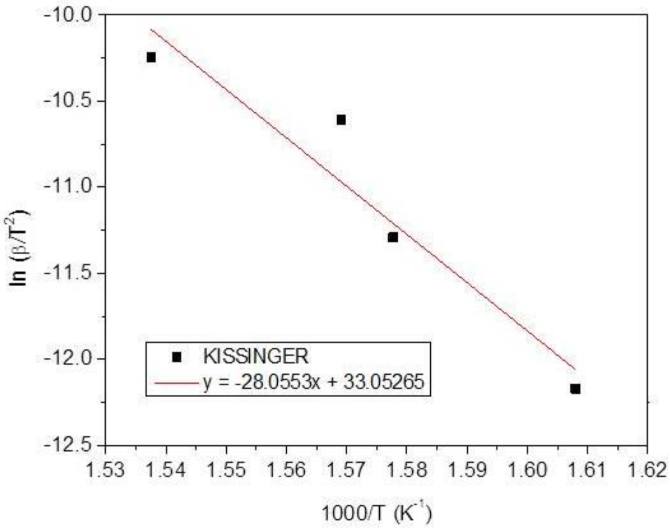

Fig. 3. Kissinger plot of *Senegalia gaumeri*

Table 4. Activation Energies and Frequency Factors for the Species Collected

Scientific Name	Activation Energy (kJ/mol)	Frequency Factor (min^{-1})
S. gaumeri	233	6.35 E+15
H. albicans	149	5.53 E+08
L. latisiliquum	185	8.81 E+11
C. glabellus	159	2.91 E+09
L. yucatanensis	138	6.62 E+07
N. emarginata	204	1.92 E+13

CONCLUSIONS

1. Six tree species representatives from the Yucatán forests were evaluated for energy purposes. The chemical compositions of the species were similar to that of other tropical species. There were species with high contents of extractables (17% to 28%), contents of holocellulose from 53% to 63%, and high contents of ash (> 5%). Low lignin contents (17% to 24%) were obtained because young branches were used.
2. The values of higher heating values, calculated from the elemental analysis, were of 16,800 to 18,500 kJ/kg, which were among the values reported for materials used as firewood.
3. The chemical composition, calorific value, and some physical properties, such as the density of these species influenced the different thermochemical processes (combustion, pyrolysis, and gasification) for the use of these plant species in the production of bioenergy. Thus, the species *S. gaumeri* and *L. yucatanensis* had the highest values of FVI of 4,780 and 4,160, respectively, due to their high calorific values and densities, as well as their low ash contents. These properties make these species attractive for use as firewood (combustion), which is the traditional way of using these species in the rural area of the Yucatán. The high ash content affected the pyrolysis and

gasification processes, and thus, the species must be evaluated in these processes to identify the most attractive species for them.

4. Obtaining the kinetics of pyrolysis by thermal analysis could serve as a criterion to select the most appropriate species for the gasification process because pyrolysis is one of the stages of gasification. The kinetic parameters can be used to model this process. The species *L. yucatanensis* and *H. albicans* presented the lowest values of activation energy, indicating that these species require less energy to initiate their thermal decomposition, and their pyrolysis occurred at lower temperatures, so they could be more suitable for use in the gasification process. However, it is necessary to perform the gasification of these species to corroborate the relationship between the kinetic parameters and the gasification process.

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REFERENCES CITED

Abbot, P. G., and Loworeb, J. D. (1999). “Characteristics and management potential of some indigenous firewood species in Malawi,” *Forest Ecology and Management* 119(1-3), 111-121. DOI: 10.1016/S0378-1127(98)00516-7

Arnold, J. E. M., Köhlin, G., and Persson, R. (2006). “Woodfuels, livelihoods, and policy interventions: Changing perspectives,” *World Development* 34(3), 596-611. DOI: 10.1016/j.worlddev.2005.08.008

ASTM D871-82 (2013). “Standard test method for moisture analysis of particulate wood fuels,” ASTM International, West Conshohocken, PA.

ASTM D1102-84 (2013). “Standard test method for ash in woods,” ASTM International, West Conshohocken, PA.

Bailis, R., Drigo, R., Ghilardi, A., and Masera, O. (2015). “The carbon footprint of traditional woodfuels,” *Nature Climate Change* 5, 266-272. DOI: 10.1038/NCLIMATE2491

Basu, P. (2013). “Biomass characteristics,” in: *Biomass Gasification and Pyrolysis, Practical Design,* Academic Press, London, U.K. DOI: 10.1016/C2009-0-20099-7

Blackie, R., Baldauf, C., Gautier, D., Gumbo, D., Kassa, H., Parthasarathy, N., Paungarten, F., Sola, P., Pulla, S., Waeber, P., *et al.* (2014). *Tropical Dry Forests: The State of Global Knowledge and Recommendations for Future Research,* Discussion paper, Centre for International Forestry Research (CIFOR), Bogor, Indonesia.

Balogun, A. O., Lasode, O. A, and McDonald, A. G. (2014). “Thermo-analytical and physico-chemical characterization of woody and non-woody biomass from agro-ecological zone in Nigeria,” *BioResources* 9(3), 5099-5113. DOI: 10.15376/biores.9.3.5099-5113

Francis, H. E., and Lloyd, W. G. (1983). “Predicting heating values from elemental composition,” *Journal of Coal Quality* 2(2), 21-25.

Cardoso, M. B., Ladio, A. H., Dutrus, S. M., and Lozada, M. (2015). “Preference and calorific value of fuelwood species in rural populations in northwestern Patagonia,” *Biomass & Bioenergy* 81, 514-520. DOI: 10.1016/j.biombioe.2015.08.003

Daniels, A. E., Painter, K., and Southworth, J. (2008). “Milpa imprint on the tropical dry forest landscape in Yucatán. Mexico: Remote sensing & field measurement of edge vegetation,” *Agriculture, Ecosystems & Environment* 123(4), 293-304. DOI: 10.1016/j.agee.2007.07.003

De los Rios, I. (2010). “El uso y aprovechamiento de leña ¿amenaza a la biodiversidad? [The use and exploitation of firewood. Threat to biodiversity?],” in: *Biodiversidad y Desarrollo Humano en Yucatán* [*Biodiversity and Human Development in Yucatán*], R. Durán-Garcia and M. E. Méndez-González (eds.), CICY, Mérida, México, pp. 362-363.

Demirbas, A. (2009). “Biofuels securing the planet’s future energy needs,” *Energy Conversion and Management* 50(9). 2239-2249. DOI: 10.1016/j.enconman.2009.05.010

Díez, H. E., and Pérez, J. F. (2017). “Physicochemical characterization of representative firewood species used for cooking in some Colombian regions,” *International Journal of Chemical Engineering* 2017, Article ID 4531686. DOI: 10.1155/2017/4531686

Ezhumalai, R., and Kumar, R. (2017). “Study on chemical, elemental and gasification characteristics of *Lantana camara* wood,” in: *Wood is Good. Current Trends and Future Prospects in Wood Utilization*, K. K. Pandey, V. Ramakantha, S. S. Chauhan, and A. N. Arun Kumar (eds.), Springer Singapore, Singapore, pp. 403-409. DOI: 10.1007/978-981-10-3115-1_38

Food and Agriculture Organization (FAO) (2018). “Forest products statistics,” (http://www.fao.org/forestry/statistics/80938/en/), Accessed 15 June 2018.

García, R., Pizarro, C., Lavín, A. G., and Bueno, J. L. (2014). “Spanish biofuels heating value estimation. Part I: Ultimate analysis data,” *Fuel* 117(Part B), 1130-1138. DOI: 10.1016/j.fuel.2013.08.048

Ghilardi, A., Bailis, R., Mas, J. F., Skutsch, M., Elvir, J. A., Quevedo, A., Masera, O., Dwivedi, P., Drigo, R., and Vega, E. (2016). “Spatiotemporal modelling of fuelwood environmental impacts: Towards improved accounting for non-renewable biomass,” *Environmental Modelling & Software* 82, 241-254. DOI: 10.1016/j.envsoft.2016.04.023

González-Iturbe, J. A., Olmsted, I., and Tun-Dzul, F. (2002). “Tropical dry forest recovery after long term Henequen (sisal. *Agave fourcroydes* Lem.) plantation in northern Yucatán. Mexico,” *Forest Ecology and Management* 167(1-3), 67-82. DOI: 10.1016/S0378-1127(01)00689-2

Hartter, J., Lucas, C., Gaughan, A. E., and Aranda, L. L. (2008). “Detecting tropical dry forest succession in a shifting cultivation mosaic of the Yucatán Peninsula. Mexico,” *Applied Geography* 28(2), 134-149. DOI: 10.1016/j.apgeog.2007.07.013

Heltberg, R. (2004). “Fuel switching: Evidence from eight developing countries,” *Energy Economics* 26(5), 869-887. DOI: 10.1016/j.eneco.2004.04.018

Hoffmann, H., Uckert, G., Reif, C., Müller, K., and Sieber, S. (2015). “Traditional biomass energy consumption and the potential introduction of firewood efficient stoves: Insights from western Tanzania," *Regional Environmental Change* 15(7), 1191-1201. DOI: 10.1007/s10113-014-0738-1

Kan, T., Strezov, V., and Evans, T. J. (2016). "Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters," *Renewable and Sustainable Energy Reviews* 57, 1126-1140. DOI: 10.1016/j.rser.2015.12.185

Kataki, R., and Konwer, D. (2001). "Fuelwood characteristics of some indigenous woody species of north-east India," *Biomass & Bioenergy* 20(1), 17-23.

Kataki, R., and Konwer, D. (2002). "Fuelwood characteristics of indigenous tree species of north-east India," *Biomass & Bioenergy* 22(6), 433-437.

Moya, R., and Tenorio, C. (2013). "Fuelwood characteristics and its relation with extractives and chemical properties of then fast-growth species in Costa Rica," *Biomass & Bioenergy* 56, 14-21. DOI: 10.1016/j.biombioe.2013.04.013

Naeher, L. P., Brauer, M., Lipsett, M., Zelikoff, J. T., Simpson, C. D., Koenig, J. Q., and Smith, K. R. (2007). "Woodsmoke health effects: A review," *Inhalation Toxicology* 19(1), 67-106. DOI: 10.1080/08958370600985875

Nasser, R. A., and Aref, I. M. (2014). "Fuelwood characteristic of six *Acacia* species growing wild in the southwest of Saudi Arabia as affected by geographical location," *BioResources* 9(1), 1212-1224. DOI: 10.15376/biores.9.1.1212-1224

Oluoti, K., Richards, T., Doddapaneni, T. R. K., and Kanagasabapathi, D. (2014). "Evaluation of the pyrolysis and gasification kinetics of tropical wood biomass," *BioResources* 9(2), 2179-2190. DOI: 10.15376/biores.9.2.2179-2190

Pachauri, S., and Spreng, D. (2011). "Measuring and monitoring energy poverty," *Energy Policy* 39(12), 7497-7504. DOI: 10.1016/j.enpol.2011.07.008

Panwar, N. L., Kothari, R., and Tyagi, V. V. (2012). "Thermo chemical conversion of biomass - Eco friendly energy routes," *Renewable & Sustainable Energy Reviews* 16(4), 1801-1816. DOI: 10.1016/j.rser.2012.01.024

Patra, T. K., and Sheth, P. N. (2015). "Biomass gasification models for downdraft gasifier: A state-of-the-art review," *Renewable & Sustainable Energy Reviews* 50, 583-593. DOI: 10.1016/j.rser.2015.05.012

Pettersen, R. C. (1984). "The chemical composition of wood," in: *The Chemistry of Solid Wood Solid,* R. Rowell (ed.), American Chemical Society, Washington D.C., USA. DOI: 10.1021/ba-1984-0207.ch002

Quiroz-Carranza, J., and Orellana, R. (2010). "Uso y manejo de leña combustible en viviendas de seis localidades de Yucatán. México [Use and management of fuelwood in dwellings in six locatities in Yucatan, Mexico]," *Maderas y Bosques* 16(2), 47-67.

Rai, Y. K., Chettri, N., and Sharma, E. (2002). "Fuel wood value index of woody tree species from Mamlay watershed in South Sikkim, India," *Forests, Trees and Livelihoods* 12(3), 209-219. DOI: 10.1080/14728028.2002.9752425

Ruiz-Mercado, I., and Masera, O. (2015). "Patterns of stove use in the context of fuel–device stacking: Rationale and implications," *EcoHealth* 12, 42-56. DOI: 10.1007/s10393-015-1009-4

SEMARNAT (2014). *Inventario Estatal Forestal y de Suelos. Yucatán 2013* [*State Forestry and Soil Inventory. Yucatán 2013*], Secretaría de Medio Ambiente y Recursos Naturales (SEMARNAT) and Comisión Nacional Forestal (CONAFOR) [Ministry of Environment and Natural Resources (SEMARNAT) and National Forestry Commission (CONAFOR)], México, México.

Slopiecka, K., Bartocci, P., and Fantozzi, F. (2012). "Thermogravimetric analysis and kinetic study of poplar wood pyrolysis," *Applied Energy* 97, 491-497. DOI: 10.1016/j.apenergy.2011.12.056

Tag, A. T., Duman, G., Ucar, S., and Yanik, J. (2016). "Effects of feedstock type and pyrolysis temperature on potential applications of biochar," *Journal of Analytical and Applied Pyrolysis* 120, 200-206. DOI: 10.1016/j.jaap.2016.05.006

TAPPI T204 cm-07 (2007). "Solvent extractives of wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T207 cm-99 (1999). "Water solubility of wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T222 om-11 (2011). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

Urquiza-Haas, T., Dolman, P., and Peres, C. A. (2007). "Regional scale variation in forest structure and biomass in the Yucatan Peninsula. Mexico: Effects of forest disturbance," *Forest Ecology and Management* 247(1-3), 80-90. DOI: 10.1016/j.foreco.2007.04.015

Valerio, F. (2012). "Environmental and health impacts of wood combustion to produce heat and power," *Epidemiologia e Prevenzione* 36(1), 16-26.

Van der Kroon, B., Brouwer, R., and Van Beukering, P. J. H. (2013). "The energy ladder: Theoretical myth or empirical truth? Results from a meta-analysis," *Renewable & Sustainable Energy Reviews* 20, 504-513. DOI: 10.1016/j.rser.2012.11.045

White, J. E., Catallo, W. J., and Legendre, B. L. (2011). "Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies," *Journal of Analytical and Applied Pyrolysis* 91(1), 1-33. DOI: 10.1016/j.jaap.2011.01.004

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