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Characterization of Lignocellulosic Biofuels by TGA

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Abstract – *Four types of biomass for use as biofuels were selected (pellets, shelled pine sawdust, rice and Rumex tianschanicus) and analyzed with a TA Instrument TGA Q500IF to define the three main components content (hemicellulose, cellulose and lignin). Runs were carried out under pyrolysis conditions and by means an algorithm implemented with Scilab tool. Therefore, the main objective was to develop a tool to determine parameters such as ash content, moisture content, amount of char, and content of hemicellulose, cellulose and lignin for combustion reactor from thermogravimetric analysis. This tool will be later integrated into a rigorous model that allows predicting the behavior of alternative biomass combustion plant residues.*

***Keywords**: Cellulose, Hemicellulose, Lignin, Thermogravimetric Analysis*

I. Introduction

Currently biomass has been receiving increasing interest as a renewable energy source in the context of climate change and mitigation of impacts. This renewable energy is based on short-cycle crops and energy crops which could contribute to the energy needs of modern society. According to the type of raw material used and applied conversion technology, biofuels can be divided into two main categories of first and second generation (and the potential of the third) of biofuels [1].

Biomass is a general term for all organic materials derived from plants. From the chemical viewpoint is a composite material, constituted by a mixture of hemicellulose, cellulose, lignin and extracts, and affected by the chemical structure of the species [2]. Today it is of second energy source, with a contribution of 14% of the world energy consumption, in comparison to the 12% provided by coal and 15% corresponding to gas [1], [3].

As since that biomass is primarily composed of hemicellulose, cellulose and lignin, it can be decomposed at a temperature range of 225-325, 305-375 and 250-500 °C, respectively [4], [5]. Similarly it has been determined that cellulose is much higher than that corresponding to lignin, which makes a larger amount of cellulose become more volatile [3], [5]. This leads to the fact that the bigger the lignin composition, the greater the amount of char produced or carbonaceous residues, because of a lower thermal degradation.

Lignocellulosic HHV of the four types of biomass found in literature are shown in Table I, where it can be seen that both pellets as sawdust have a high HHV. It is also noteworthy the high content of hemicellulose and cellulose, compared with rice husk.

In general, biomass combustion models can be classified as macroscopic and microscopic. The macroscopic properties of the biomass are characterized by elemental analysis, calorific value, moisture content, particle size, bulk density and melting temperature of ashes. The analysis for determine the microscopic properties include thermal and kinetic data of minerals [19].

TABLE I
LIGNOCELLULOSIC COMPOSITION AND HHV OF THE DIFFERENT BIOMASS IN THE LITERATURE

Biomass	Hemicellulose	Cellulose	Lignin	HHV	Reference
Rice Husk	18-31%	25-43%	14-30%	15,84 MJ/kg	[6], [7], [8]; [9] [10]
Sawdust	25-34%	43-46%	26-28%	21 MJ/kg	[9], [11], [12], [13], [8]
Pellets	20-27%	39-44%	28-32%	19 MJ/kg	[14], [15], [16], [17]
Rumex				12,17 MJ/kg	[18], [14], [16]

Biomass has important advantages as a raw material for combustion; due to the high volatility of the fuel and the high reactivity of both the fuel and the resultant char. Gravimetric techniques (isothermal and nonisothermal) have generally been used to investigate the reactivity of the carbonaceous materials [19], [20]. these techniques, has been selected in this work to evaluation physical and chemical properties, generating a variety of correlations that predict the optimal conditions for these types of biomass which can be applied as biofuels [19]. Moreover a number of correlations have been evaluated to predict the heating value from proximate analysis. Similarly [21] proposed a tool that allowed the calculation from a quick scan of the calorific value from proximate analysis.

This work aims to design a versatile and reliable tool for calculating, from an easy and fast analysis like proximate analysis, other properties related to solid biofuel quality, such as lignocellulosic composition. This tool will be later integrated in a rigorous model, which will allow the prediction of the combustion behavior of alternative waste plant biomass.

II. Experimental

Four different kinds of biomass have been identified and characterized: (1) pellets, (2) pine sawdust (pinus insignis), (3) rice husk and (4) rumex tianschanicus (herb). Each sample has been analyzed by TGA Q500IF of TA Instrument (Figure 1).

In order to define the three stages corresponding to the three main components, DTG curves have been analyzed by means of an algorithm implemented in Scilab. The flow char is presented in Figure 2.

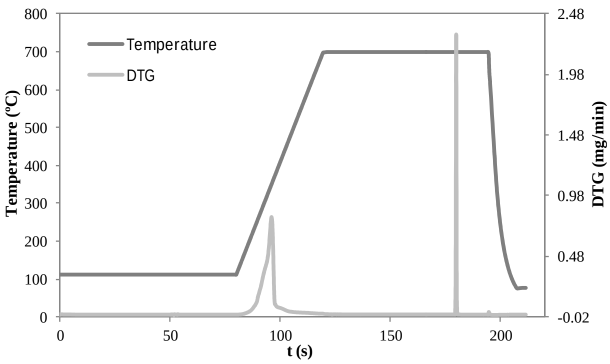

Fig. 1. DTG curve obtained in the test performed at ramp 15 ºC/minute

III. Results

Generally, in the kinetic schemes of multiple stages, it is considered that the pyrolysis process is the sum of three independent reactions occurring in parallel, without any interaction between them, corresponding to the degradation of hemicellulose, cellulose and lignin [22]-[24]. Although there are significant interactions between degradation of the three components, the thermogravimetric analysis shows three distinct peaks corresponding to the identification of each degraded compound.

Figure 3 shows the deconvolution of sawdust pine, where it can be observed a main peak associated with cellulose, a left shoulder associated with the hemicellulose and a smaller peak at the right associated with the lignin descomposition.

From the three curves obtained (hemicellulose, cellulose and lignin) for the four biomass, it can be concluded that in the case of pine sawdust and pellets, lignin and hemicellulose are the first to degrade. However lignin is not completely degraded until high temperatures, pyrolysis occurs at a narrow range of temperatures, resulting in a high, narrow peak [25].

In the case of rice husk and rumex, the three components begin degrading process starts, hemicellulose is the first degrading completely, and followed by hemicellulose and lignin which degradation continues at high temperatures (Figure 4).

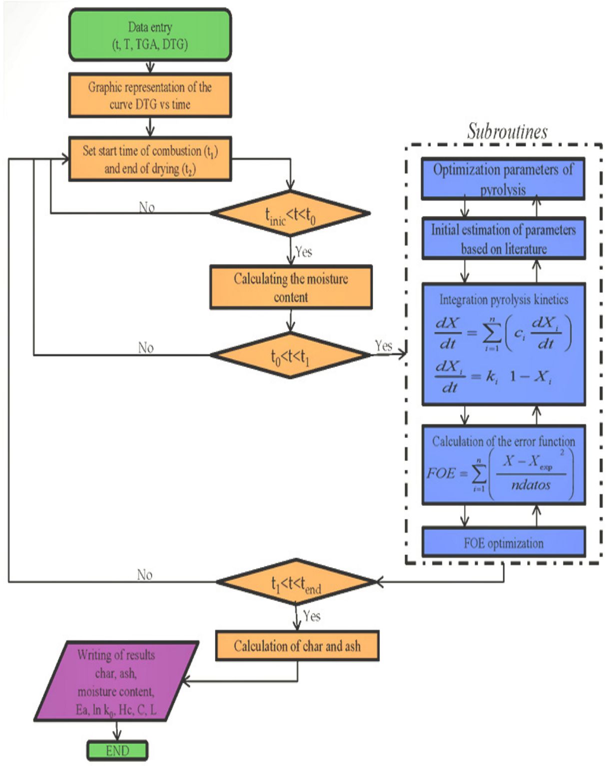

Fig. 2. Flowchart of the tool used for processing the data

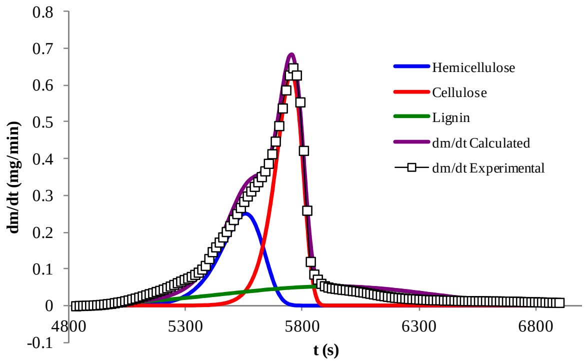

Fig. 3. Adjustment by deconvolution of the three components of pine sawdust

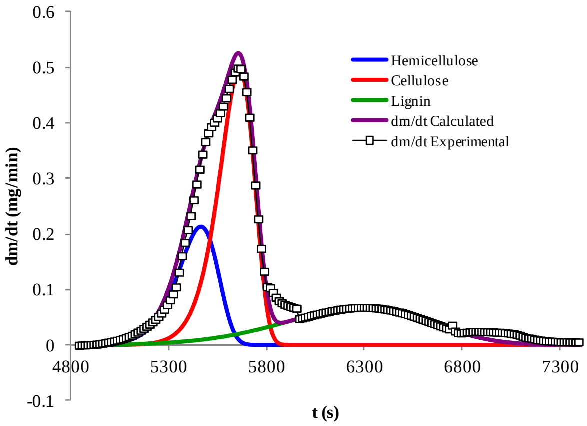

Fig. 4. Adjustment by deconvolution of the three components of rice husk

Table II shows the measured content of hemicellulose, cellulose and lignin of the four types of biomasses, in which rumex is especially noteworthy with a high content of cellulose which allows the formation of volatile compounds making conferring suitable conditions for biomass combustion. The contents of cellulose, hemicellulose and lignin of pine sawdust and rice hulls are very similar to those obtained by other authors [10], [13].

TABLE II
CONTENT OF HEMICELLULOSE, CELLULOSE AND LIGNIN

Biomass	Hemicellulose	Cellulose	Lignin
Rumex	15.04	59.18	15.62
Sawdust	21.94	35.67	33.07
Rice Husk	19.87	27.66	24.68
Pellets	21.71	39.59	34.50

Table III shows the values of activation energy (Ea) and preexponential factor (k_0) corresponding to the three parallel reactions for the degradation of hemicellulose, cellulose and lignin of the four treated biomass. The results of sawdust and rice husk are consistent with other work [26]-[28].

TABLE III
PREEXPONENTIAL FACTORS AND ACTIVATION ENERGIES

Biomass	Calculated value	Hemicellulose	Cellulose	Lignin
Rumex	ln k_0 (s^{-1})	±10.99	±14.66	±3.98
	Ea (kJ mol^{-1})	±65.30	±95.24	±55.93
Sawdust	ln k_0 (s^{-1})	±20.22	±38.96	±-1.11
	Ea (kJ mol^{-1})	±117.37	±221.53	±28.25
Rice husk	ln k_0 (s^{-1})	±14.65	±32.65	±1.38
	Ea (kJ mol^{-1})	±88.11	±183.26	±39.41
Pellets	ln k_0 (s^{-1})	±21.53	±32.28	±-4.96
	Ea (kJ mol^{-1})	±120.99	±186.89	±11.30

IV. Discussion

In Figure 5 it can be seen that the results obtained in the deconvolution of the different biomass are satisfactory, since there is a high relationship between the biomass treated and those found in the literature. On the other hand, [8] made a classification in six different groups according to the composition, denoted for:CHL, HCL, HLC, LHC, LCH and CLH. Each point in the given sector is characterized by the consecutive decreasing amounts of the three components. For example, in CHL sector, concentrations vary following the structural order: cellulose> hemicellulose> lignin. In this sense rumex and rice husk are in the CHL area, while the pellets are in the CLH group and sawdust in the boundary between the CLH and CHL sectors.

The kinetic results obtained for pine sawdust are very similar to those obtained by other authors [26], with values of activation energy of 115 ±9 kJ mol^{-1} for hemicellulose, 218 ±15 for cellulose and 35 ±2 for lignin.

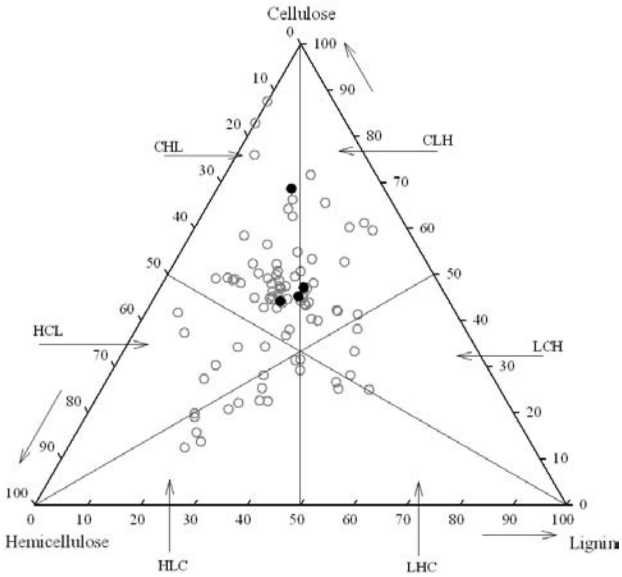

Fig. 5. Ternary composition diagram of hemicellulose, cellulose and lignin of different biomass

These authors applied lineal adjustment to the data obtained from the pyrolysis of rice husk using the linearization of the kinetic equations, introducing an additional step for drying. The values of activation energy obtained are very similar to those obtained in this work of 48, 199 and 34 kJ mol^{-1} of hemicellulose, cellulose and lignin, respectively [27], [28].

V. Conclusion

TGA analysis allows a better of the raw material, optimum heating ramp to perform an adequate degradation of the three components (hemicellulose, cellulose and lignin) with a previous drying step, biomass which allows moisture loss and give better combustion conditions. Moreover, high temperatures are optimal isothermal period, allowing the complete degradation of lignin content, then move to a stage of oxidation at high temperatures by burning the char formed by the pyrolysis process.

This tool allows test and reliable lignocellulosic analysis from a thermobalance analysis. This may be of particular interest in the context of more sophisticated and expensive equipment for experimental measurement as is the analysis of hemicellulose, cellulose and lignin.

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