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Higher Heating Values of hydrotropic, hydrolytic and alkaline lignin from grape seeds and other types of biomass

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INFORMAN,

Que D^a. MARÍA PINILLA DE DIOS ha realizado bajo nuestra dirección el Trabajo Fin de Máster, del Máster en Investigación Ingeniería de Procesos y Sistemas, titulado *“Higher Heating Values of hydrotropic, hydrolytic and alkaline lignin from grape seeds and other types of biomass”*.

Valladolid, 7 de Septiembre de 2012

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Reunido el Tribunal designado por el Comité Académico del Máster en Investigación en Ingeniería de Procesos y Sistemas, para la evaluación de los Trabajos Fin de Máster, y después de estudiar la memoria y atender a la defensa del trabajo "*Higher Heating Values of hydrotropic, hydrolytic and alkaline lignin from grape seeds and other types of biomass*", presentado por la alumna D^a. MARÍA PINILLA DE DIOS, decidió otorgarle la calificación de _____.

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HIGHER HEATING VALUES OF HYDROTROPIC, HYDROLYTIC AND ALKALINE LIGNIN FROM GRAPE SEEDS AND OTHER TYPES OF BIOMASS

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ABSTRACT

Lignin is a natural polymer aromatic-based that exhibit interesting application both as a final product and as a source of energy and aromatic compounds. For decades lignin has been a discarded sub product of the pulp industry (black liquor) used basically as energy source for the pulp mill, creating a number of environmental problems. Currently a number of production processes are available, i.e. alkaline extraction, Kraft, organosolv, hydrotrope extraction, hydrolysis in sub and supercritical water, for instance. The Higher Heating Value (HHV) is a required parameter for the characterization of the biomass fractions. There are techniques to estimate HHV using the elemental composition and other parameters, but this is an indirect method and requires the availability of the analytical techniques. In this work we determine the HHV of three types of lignin, alkaline (19.82 kJ/g), hydrotropic (26.54 kJ/g) and from subcritical water hydrolysis (26.19 kJ/g), also cellulose (16.31 kJ/g), anhydrous glucose (15.64 kJ/g), grape seeds (18.84 kJ/g) and extracted grape seeds (23.78 kJ/g) by using an adiabatic combustion calorimeter and a combustion bomb. We propose the use of cellulose as agglomeration agent for the biomass and lignin, simplifying the pellet preparation process. Calibrations repeatability for a standard of Benzoic Acid was 1.9% and for a standard of Anhydrous Glucose was 3.4%. Finally, the average from calibrations was 2.6%.

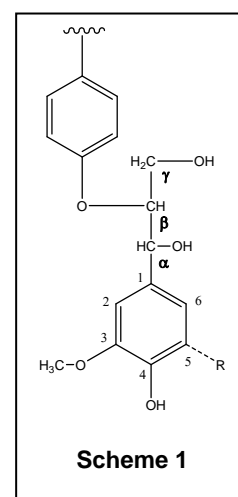
Keywords: Lignin, calorimeter, subcritical water hydrolysis, heat of combustion, depolymerization

1. INTRODUCTION

Nowadays, due the population growth, the GHG-derived (greenhouse gases) problems and global economic restrictions there is an increased social need of environmental protection and petroleum-substitutes. Biomass has been used for centuries as energy source, although the petroleum hegemony during the last two centuries has modified this vision completely. The need of a global carbon balance has motivated seeking for novel strategies for the more efficient use of natural biomass. In the last decade a great effort has been done in the research of biofuel production, such as bioethanol, biodiesel, etc. (Bozell 2008; Cheng and Zhu 2009) Nevertheless there is still not a clear option, as three generations of biofuels have appeared in less than one decade based on the starting materials, i.e. first sugar & natural oil, second surplus biomass and third algae-based biofuels.

Lignin is a natural amorphous polymer that acts as glue for plants, giving structural integrity, and as a barrier to evaporation allowing the efficient transfer of water through the plant (Heitner, Dimmel et al. 2010). Lignin is a complex aromatic-base polymer (see Scheme 1) composed by the polymerization of three alcohols, i.e. p-coumaryl alcohol, conypheryl alcohol y sinapyl alcohol. The aromatic rings create three main groups, i.e. guaiacyl, syringyl y p-hydroxyphenyl. Lignin is a subproduct of pulp and it is normally used to move the pulp mill (black liquor) in the Kraft process. However there are other processes to produce pure lignin as a product or as an energy source, as it will be commented next.

Hydrolysis consist in treating biomass in aqueous medium at subcritical and supercritical conditions to achieve degrade it and separate it into various components for subsequent use (Kruse and Gawlik 2003). The reaction takes place at temperatures between 330-410 ° C and pressures between 30-50 MPa. The main components identified are phenols, furfurals, acids and aldehydes. Also, they studied the degradation



of biomass studying its TOC (total organic carbon) and the composition of the gas phase formed, as the properties of water in sub and supercritical conditions differ and hence, the degradation of the biomass will also be different. Other researches have used biomass fractions, such as lignin (one of the three fractions of lignocellulosic biomass) from various sources, for example, have been extracted lignin and its fractions from cotton, to compare fractions of lignin dissolving them in different systems, so that they get isolate it and study it. (Meng, Kang et al. 2012). Solutions like LiCl/DMAc, TABF/DMSO, NaOH/urea/H₂O₂, etc., were used, but the ionic liquid exhibiting higher efficiency than the rest of the system was [Amim]-Cl/DMSO. Their results exhibit that lignin fractions possessed higher purities and molecular weights than milled wood lignin (MWL). More studies, investigated, too (Meng, Kang et al. 2012), about biomass recalcitrance, the natural resistance of plant cell walls to microbial and enzymatic deconstruction (Himmel, Ding et al. 2007). Lignocellulosic biomass with low lignin quantity, e.g. straw, is recognized as a source of sugar for fermentation to biofuels.

From biomass, it is also possible to generate added value products such as bio-oils and bioalcohols, which would allow their incorporation thereof in industry, such as biorefineries (Meng, Kang et al. 2012). For production biofuel, there are some studies, such as the review of (Peterson, Vogel et al. 2008), in which converting biomass into liquid and gaseous fuels has been studied in sub- and supercritical water technologies, technologies, in which temperatures are between 200-600°C and pressures, between 5-40 MPa. They studied liquefaction processes in a range of lower temperature reactions (200°C–400°C) getting liquid products, bio-oil or bio-crude. Moreover, the gasification processes taking place at higher temperatures in the range of 400°C-700°, can produce methane or hydrogen gases in high yields.

The calorific value of a fuel is the quantity of heat produced by its combustion. Combustion processes generate water vapor. The Higher Heating Value (HHV) takes into account that the water of combustion is entirely condensed so the heat extracted by the vapor production is recovered. HHV is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced. A standard temperature of 25°C is normally used (as is used in this study).

On the other hand, the Lower Heating Value (LHV) takes into account that the products of combustion contain water vapor and the heat in the water vapor is not recovered. LHV is determined by subtracting the heat of vaporization of the water vapor from the HHV. The LHV is useful for determining the useful extractable energy in an open combustion for instance.

Measuring the heat of combustion of a sample is then essential to characterize it, in terms of energetic power. For this purpose, in this work we have used a combustion bomb inside an adiabatic combustion calorimeter. Thus, fulfilling the first postulate of Thermodynamics (existence of the thermodynamic equilibrium state) and the first principle of Thermodynamics (energy conservation law), it is going to work at any moment ensuring adiabatic conditions.

There are several studies, in which it is innovating in the design and operation of the bomb (Albert 1998) and the combustion type calorimeter (Xu-Wu and Jun 2000). However, there are numerous compounds which are not known their heat of combustion. Because of that, this paper is going to show the heat of combustion of some of them for a further characterization and, also, it is going to show an innovative form of agglomeration of the samples for subsequent ignition.

Several authors (Nhuchhen and Abdul Salam 2012) have studied the HHV of different biomass through linear correlation with HHV in the range of 5.63-23.46 kJ/g. Biomass such as coal and other solid fuels, comparing them to a large list of biomass materials. There are other authors who have been investigating on different types of correlation, (Cordero, Marquez et al. 2001). Equation tested on lignocellulosic wastes and chars from carbonization processes, at different temperatures (300°C-700°C). The heating values calculated have a deviation below 2%, and other authors,(Sheng and Azevedo 2005), also studied different correlations. They studied a correlation between the higher heated value and the dry ash content of biomass. This formula has an accuracy which shows than 90% of the predictions have a $\pm 5\%$ error. There are some studies that have been estimating the calorific value of the forest fuel by forest biomass: wood, oil, coal, natural gas and peat with several economic aspects (Lyons, Lunny et al. 1985). Some studies, (Demirbaş 1997) y (Demirbaş 2001), researched about calculating the higher heated values of biomass and the relationship between the content of lignin and the heating values of biomass. In both studies, several samples were studied with linear correlations.

In this work our aim is to study three types of lignin, one commercial (alkaline) and two research lignin samples (from a hydrotropic process at Abo Academy and from a subcritical water hydrolysis process at the University of Valladolid). The main problem to solve is how to prepare the pills, as the lignin does not

agglomerate properly. We want to compare the values of the three lignin samples as they have not been determined before.

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2. MATERIALS AND METHODS

2.1. Material

The materials employed during the experimentation were the following: lignin samples used in this study are hydrotropic lignin (from Åbo Akademy, *Finland*), alkaline lignin (a commercial lignin from *Aldrich Chemistry, Spain*) and from subcritical water hydrolysis lignin. Grape seeds are from *Valladolid, Spain*. Cellulose is cellulose microcrystalline (from *Alfa Aesar, Germany*). The Glucose used in this study, glucose anhydrous, was purchased from *VWR* and the Benzoic acid is from *Panreac, Monplet & Estenan S.L., Barcelona (Spain)*. The fuse wire is from *Parr, U.S.A* and, finally, the compressed oxygen cylinder was purchased from *Carbuos Metálicos S.A., Barcelona (Spain)*.

2.2. Experimental setup

The equipment used consists on a press for making pellets. In order to assure adiabatic conditions, a refrigerated immersion cooler and a heated water bath (*Grant Instruments (Cambridge) Ltd., England, C2G and W38*, respectively) have been used. The equipment in which the combustion takes place is the combustion bomb (*Parr Instruments CO. Moline, Ill. U.S.A*), an oxygen bomb, and the equipment that makes the combustion and keeps the adiabatic conditions before and after combustion is the adiabatic calorimeter (*Parr Instrument Company, Inc. Moline, Illinois, U.S.A*), which contains the water vessel with water and the bomb. This calorimeter has a stirrer with an electric motor to homogenize the temperature of the water vessel (*Fractional Horsepower Motor, Chicago Ill., U.S.A*). Finally, a temperature sensor, RTD, Pt-100 (*Desin Instruments, Barcelona, Spain*) with a system multimeter (*PM 2534 FLUKE and PHILIPS, Holland*) has been used to control the temperature, at every moment, especially the steady temperature before the combustion and the maximum temperature reached after combustion.

Fig.1. shows the schematic flow diagram of the system.

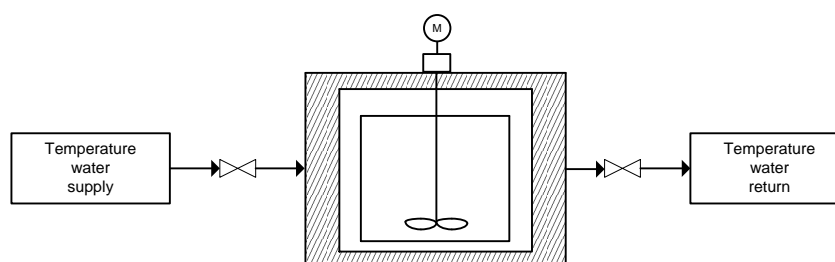


Fig. 1. Flow diagram of the process.

The temperature profiles are shown in Fig. 2

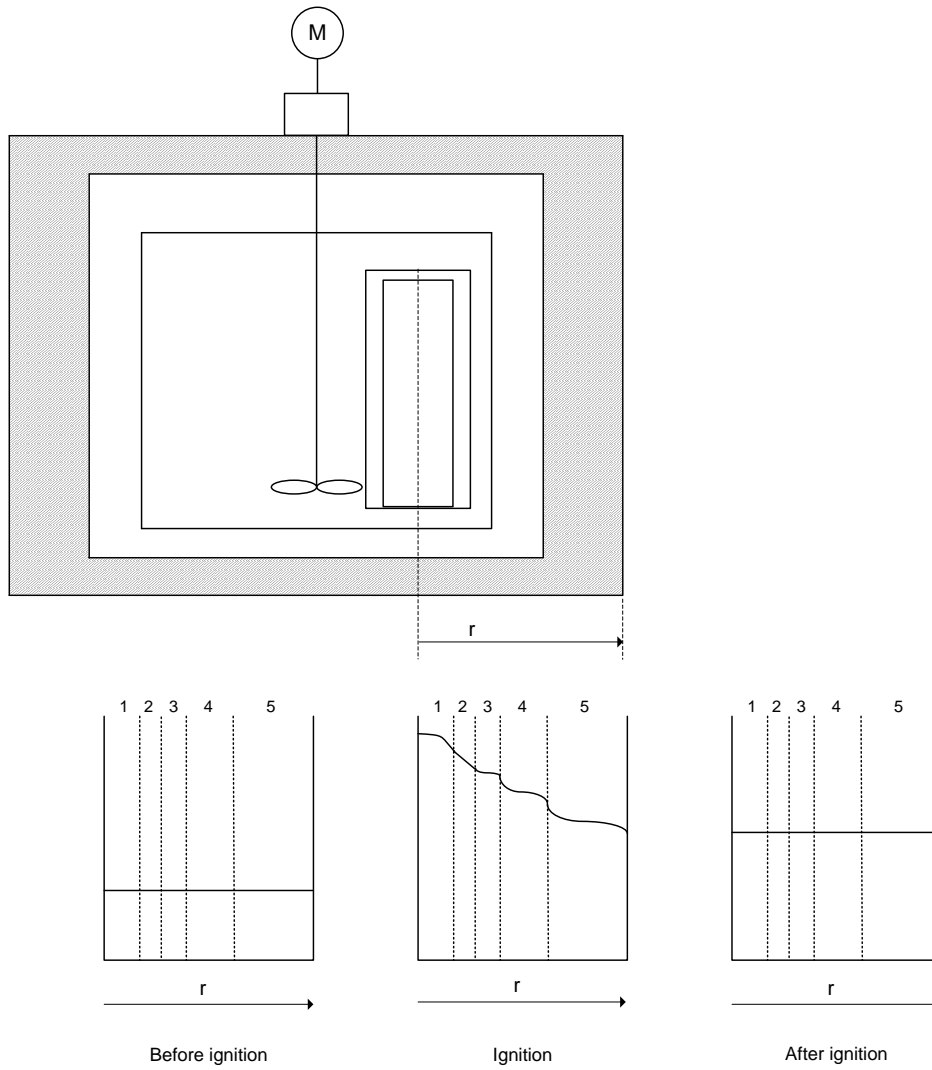


Fig. 2. Temperature profiles. 1 represents the behavior of the temperature inside the bomb; 2, temperature drop through the wall thickness of the bomb; 3, temperature drop in the water vessel; 4, temperature drop in the air gap and 5, represents the temperature drop through the jacket.

In the following figures, it is shown all the necessary equipment involved in the process. Figures 3 and 4, presents the press used to form pellets.

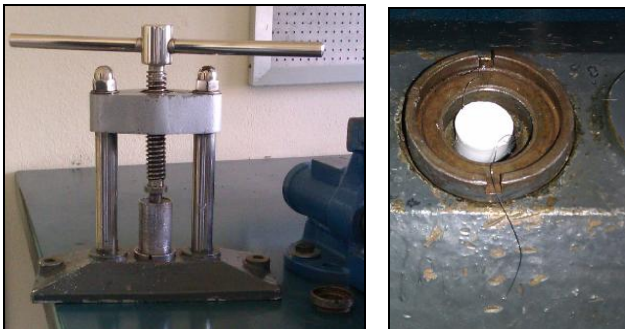


Fig. 3 y 4. Press and pellet with the fuse wire.



Fig. 5. Multimeter with a Pt-100 and a computer for monitoring the temperature.

Figure 5 represents the multimeter and the computer program used for monitoring temperatures by implementing a Pt-100. The multimeter reads the resistance values in the program, due to previous calibration of the temperature sensor, and these values are translated and recorded into temperature values.

Fig. 6 and 7 represent the heated water bath, used to adjust the temperature with the refrigerated immersion cooler and the adiabatic calorimeter used to carry out combustion, respectively.



Fig. 6 and 7. The refrigerated immersion cooler, the heated water bath and the calorimeter, respectively

It is observed in Fig. 6, that there is a temperature control system, so it can be manipulated as desired depending on the operation conditions and a refrigerated immersion cooler to ensure the stability of the temperature with the minimum of disruption as possible. In Fig 7, which shows the calorimeter, this has implemented a Pt-100, to determine the temperature at any time and it is associated with a motor which acts ensuring complete homogenization of the temperature in the water vessel; so, the heat transfer is performed in the least possible time.

Finally, since an atmosphere of oxygen is necessary for a combustion, Fig. 8 shows the bomb of combustion, where the pellet is connected to the electrodes with the fuse wire.

In Fig.8, it is seen that the bomb is within the combustion water vessel and immersed in water.



Fig. 8. Bomb of combustion with the electrodes and the water vessel inside the calorimeter.

Thus, through the jacket of the calorimeter, it is achieved that the jacket temperature is practically identical to that of the boiler water, thereby ensuring adiabatic conditions at all times.

2.3. Experimental procedure

The wire is cut and weighted before the ignition and after it, in an analytic balance (*A&D Weighing, AND HR-202, U.S.A*). The sample to burn is weighed and pressed together with the fuse wire so, as to form the pellets. After placing the pellet in the crucible and attach it to the electrodes, it is introduced into the bomb. It is closed and subjected to an oxygen atmosphere of 20 bar.

The water vessel is weighted empty and with water, ensuring that the amount of water is always similar. The bomb together with the water vessel is entered inside the adiabatic calorimeter and a Pt-100 is used to measure the temperature continuously. To avoid heat losses/gains from the ambient the refrigerant jacket temperature is controlled following the water vessel temperature by adjusting the thermal bath (the heated water bath). This bath is at a determined temperature (0.3°C) above the temperature value of the tap water, every day. Once a stable temperature is reached, the ignition takes place. The temperature of the heated water bath has to be raised (1°C) and it is expected to get the maximum temperature. Both temperatures, before the ignition and the maximum temperature reached after it, have to be recorded.

All experiments were run at least twice. A normal run requires ca. 4 hours (2 h preparation, 1 h ignition/stabilization and 1 h cleaning).

2.3.1 Temperature determination

The track of the temperatures before and after the ignition is recorded every combustion.

As shown in Figure 9, the first horizontal section indicates the temperature stability before the ignition. The sloping section indicates the increase in temperature that occurs when performing the ignition and, finally, the following horizontal section, shows the temperature stability and the maximum temperature that is reached after the ignition.

So, for each sample, it has been obtained a graph (always the same type) which shows the temperature behavior along the experiment (every 5 seconds, the program takes a measure), it has shown the stable temperature before ignition, the maximum temperature that is reached in the ignition and it has been calculated the average of both temperatures (before and after ignition), the standard deviation and the error committed.

Next one example is shown including all the calculations.

Grape seeds with Benzoic acid

First combustion

The chosen temperatures for the energy balance calculations are the following:

T _{before ignition} (°C)	22.41
T _{maxim after ignition} (°C)	24.22

Table 1. Temperatures before and after ignition.

The graph that describes the combustion behavior is:

	Before ignition	After ignition
Average (°C)	22.38	24.20
s (°C)	0.017	0.012
	0.076%	0.049%

Table 2. Validity of the set temperatures.

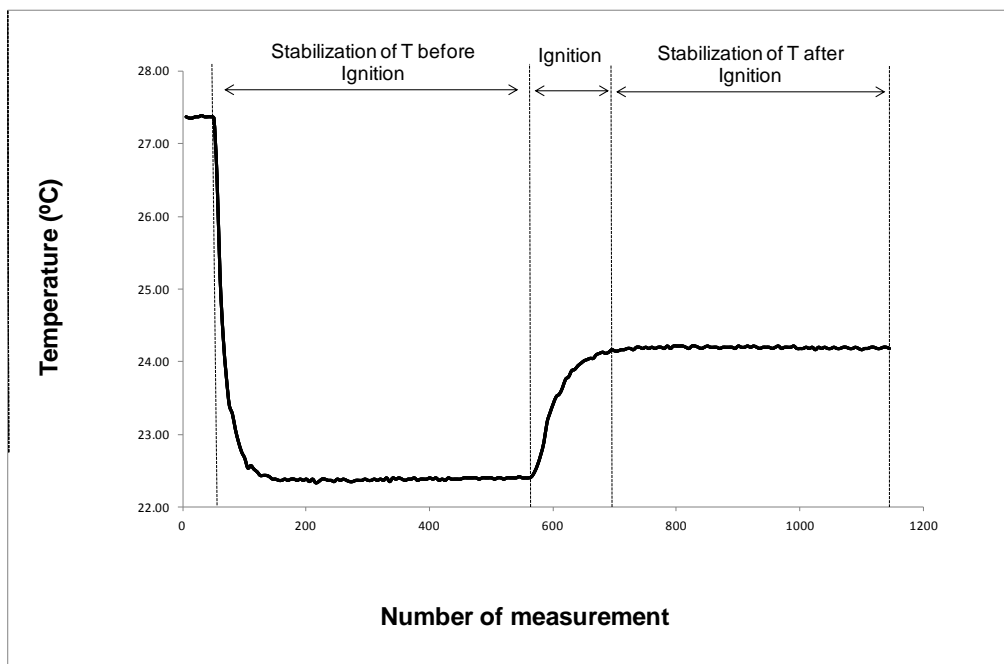


Figure 9. Behavior of the first combustion of Grape seeds with Benzoic Acid.

Second combustion

The chosen temperatures for the energetic calculations are the following:

T _{before ignition}	(°C)	23.92
T _{maxim after ignition}	(°C)	25.66

Table 3. Temperatures before and after ignition.

The graph that describes this second combustion is:

	Before ignition	After ignition
Average (°C)	23.91	25.63
s (°C)	0.012	0.014
	0.050%	0.056%

Table 4. Validity of the set temperatures.

As it can be seen, the set temperatures and average temperatures differ slightly, validating the procedure.

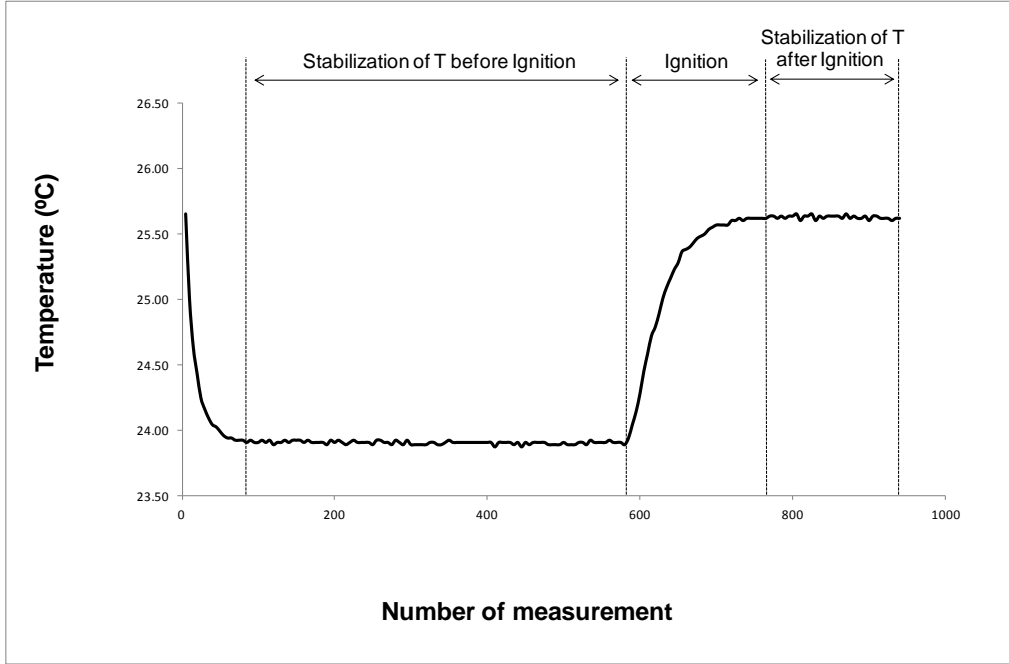


Figure 10. Behavior of the second combustion of Grape seeds with Benzoic Acid.

3. RESULTS AND DISCUSSION

3.1. Energy balance and calibration

The system behaves in a non-steady state, when the ignition occurs a great quantity of energy is released in a short period of time. The temperature inside the calorimeter is not recorded in this work and the measurement of the ignition-combustion times is out of the scope of this work. However, the non-steady balance assuming a similar T in the system is shown in eq. 1 to understand the process better.

$$(m_{\text{Water}} \cdot c_{p_{\text{water}}} + m_{\text{bomb}} \cdot c_{p_{\text{bomb}}} + m_{\text{vessel}} \cdot c_{p_{\text{vessel}}}) \cdot \frac{dT}{dt} = U_1 \cdot S_1 \cdot (T - T_{\text{amb}}) - U_2 \cdot S_2 \cdot (T - T_{\text{amb}}) \quad (1)$$

$$\delta(t_{\text{ignition}}) \cdot (m_{\text{sample}} \cdot \Delta H_{\text{comb}} + m_{\text{fuse wire}} \cdot \Delta H_{\text{fuse_wire}}) = U_1 \cdot S_1 \cdot (T - T_{\text{amb}}) \quad (2)$$

Where the term $U_1 \cdot S_1 \cdot (T - T_{\text{amb}})$ indicates the heat transferred from the combustion bomb to the water and $U_2 \cdot S_2 \cdot (T - T_{\text{amb}})$ indicates the heat transferred from the ambient (air gap) to the water.

The Dirac delta function $\delta(t_{\text{ignition}})$ is required to indicate that heat of combustion is released during a short period of time, so the equation is dimensionally correct.

The steady state balance is:

$$\sum (m_i \cdot cp_i) \cdot (T_{\text{final}} - T_{\text{initial}}) = (m_{\text{sample}} \cdot \Delta H_{\text{comb}} + m_{\text{fuse wire}} \cdot \Delta H_{\text{fuse_wire}}) - U_2 \cdot S_2 \cdot (T - T_{\text{amb}}) \quad (3)$$

$$\sum (m_i \cdot cp_i) = \frac{m_{\text{sample}} \cdot \Delta H_{\text{comb}} + m_{\text{fuse wire}} \cdot \Delta H_{\text{fuse_wire}}}{(T_{\text{final}} - T_{\text{initial}})} \quad (4)$$

Finally, the term $\sum(m_i \cdot cp_i)$ is the system calibration constant. This parameter is independent of the material to be burnt; it only depends on the equipment that constitutes the system and it is always the same.

When using a calibrating compound, such as, benzoic acid, with a known enthalpy of combustion the calibration parameter is determined.

The accuracy of the method relies in the quantity of heat losses of the calorimeter.

$$Q_{losses} = U_2 \cdot S_2 \cdot (T_{amb} - T) \quad (5)$$

where T_{amb} is a function of time, as it is controlled to follow as close as possible the water temperature (T).

In order to estimate the maximum heat losses in the system we have assumed natural convection in the air gap, a global coefficient of heat transfer, $U \approx 10 \text{ W/m}^2 \cdot \text{C}$. Taking into account the dimensions of the water vessel ($L=0.20\text{m}$, $D=0.10\text{m}$) and the average of the difference of temperature of combustion ($\Delta T = 2^\circ\text{C}$), the maximum losses that we can get, if the process were not adiabatic, are:

$$Q_{losses} = U \cdot (\pi \cdot D \cdot L) \cdot (\Delta T) = 10 \cdot (\pi \cdot 0.10 \cdot 0.20) \cdot (2) \quad (6)$$

$$Q_{loss} = 1.257 \text{ W}$$

Considering an average duration of the combustion process of 20 minutes, the result is:

$$\Delta H_{loss} = 1507.96 \text{ J} \quad (7)$$

The specific heat that it is produced in the combustion, with a value of $\Delta H_{\text{Comb Benzoic Acid}} = 26.45 \text{ kJ/g}$ and with an average value of the mass to be burnt from the calibration with Benzoic Acid, $m_{\text{Benzoic Acid}} = 0.95871 \text{ g}$, is:

$$Q_{comb} = m_{\text{Benzoic Acid}} \cdot \Delta H_{\text{Comb.Benzoic Acid}} \quad (8)$$

$$Q_{comb} = 25357 \text{ J}$$

corresponding to a maximum total energy loss of 6%. This value is still quite high, there it is necessary to control the temperature of the external water bath to follow as close as possible the inside water temperature, so a minimum energy is transferred by the air gap.

3.2. Calibrations results

The calibration constant of the system requires a standard combustion heat, and measuring the difference between the stable temperature before ignition and the maximum temperature recorded after ignition. Using eq. 9 (derived from the energy balance at steady state eq. 4), the calculation of the parameter is immediate.

$$\sum(m_i \cdot cp_i) = \frac{m_{benzoico} \cdot \Delta H_{benzoico}}{\Delta T} \quad (9)$$

For a reliable calibration, the calibration has been performed with another second standard or standard, whose heat of combustion is known. In this case, anhydrous glucose was chosen. This is agglomerated with benzoic acid, since when performing the pellets, an important amount of it, is lost; in fact, this happens even agglomerating.

Thus, using two calibrations with two different patterns, it may be get the overall error that is being committed.

3.2.1 Calibration with Benzoic Acid

Taking into account the values of the heat of combustion of the standards given in Table 5,

$\Delta H_{\text{Benzoic Acid}}$	(kJ/g)	26.45
$\Delta H_{\text{Fuse wire}}$	(kJ/g)	5.86
$\Delta H_{\text{Anhydrous glucose}}$	(kJ/g)	15.65
$\Delta H_{\text{Cellulose}}$	(kJ/g)	16.31

Table 5. Data of the heat of combustion.

the results are shown in Table 6:

N° Calibration	1	2	3	4
$m_{\text{Benzoic Acid}}$ (g)	0.94819	0.95142	0.96384	0.97137
T_{initial} (°C)	22.68	22.68	22.78	22.61
T_{final} (°C)	24.68	24.64	24.73	24.58
ΔT (°C)	2.00	1.96	1.95	1.97
m_{cp} (kJ/°C)	12.54	12.84	13.07	13.04

Table 6. Values of the calibration constant with Benzoic Acid.

3.2.2 Calibration with Glucose

The results are:

N° Calibration	1	2	3	4
m_{Glucose} (g)	0.64482	0.59977	0.63779	0.72632
$m_{\text{Benzoic Acid}}$ (g)	0.21494	0.19992	0.2126	0.24211
T_{initial} (°C)	21.97	23.73	23.03	24.61
T_{final} (°C)	23.20	24.81	24.27	26.00
ΔT (°C)	1.23	1.08	1.24	1.39
(m_{cpi}) (kJ/°C)	12.83	13.59	12.58	12.78

Table 7. Values of the calibration constant with Anhydrous Glucose.

3.3. Samples Results

Once the combustion is completed, it is going to calculate the various energetic terms of the system: the heat that the pellets transferred, the heat of the sample (without the standard and the fuse wire) and, finally, the heat of combustion of the sample.

With the previous equations, the results are shown in Table 8. In this table, there are shown the duplicates of the samples to be burnt.

Samples	Calibration Component	m _{sample} (g)	m _{calibration component} (g)	m _{fuse wire} (g)	T _{initial} (°C)	T _{final} (°C)	ΔT (°C)	Q _{pellet} (kJ)	Q _{sample} (kJ)	ΔH (kJ/g)
Grape seeds	Benzoic Acid	0.5022	0.5013	0.00978	22.41	24.22	1.81	23.30	9.98	19.88
Grape seeds	Benzoic Acid	0.5029	0.5066	0.00916	23.92	25.66	1.74	22.40	8.95	17.79
Cellulose	- -	0.9786	0.0000	0.00542	22.78	24.02	1.24	15.96	15.93	16.28
Cellulose	- -	0.9590	0.0000	0.00612	23.63	24.85	1.22	15.71	15.67	16.34
Hydrotropic lignin	Cellulose	0.6590	0.2197	0.00375	24.42	26.07	1.65	21.24	17.64	26.76
Hydrotropic lignin	Cellulose	0.7149	0.2383	0.01602	24.90	26.31	1.41	18.15	14.17	19.82
Alkaline lignin	Cellulose	0.5895	0.1965	0.01243	25.46	26.92	1.46	18.80	15.52	26.32
Hydrolytic lignin	Cellulose	0.2382	0.7145	0.00075	23.51	24.90	1.39	17.89	6.24	26.19
Extr. grape seeds	Cellulose	0.7399	0.2466	0.00105	23.54	25.22	1.68	21.63	17.60	23.78
Anhydrous Glucose	Benzoic Acid	0.7263	0.2421	0.01653	24.61	26.00	1.39	17.89	11.39	15.69
Anhydrous Glucose	Benzoic Acid	0.6448	0.2149	0.01641	21.97	23.20	1.23	15.83	10.05	15.59

Table 8. Results of several samples.

In Table 9, the results appear with the average error for each combustion:

Samples	ΔH (kJ/g)
Grape seeds	18.84 ± 0.058
Cellulose	16.31 ± 0.055
Hydrotropic lignin	26.54 ± 0.048
Alkaline lignin	19.82 ± 0.041
Hydrolytic lignin	26.19 ± 0.046
Extracted grape seeds	23.78 ± 0.047
Anhydrous Glucose	15.64 ± 0.055

Table 9. Average results of the samples with the average error of each combustion.

These are the heat capacities of the samples burned. There are tabulated values of other samples, where it can see that there are different calorific values of each. In this way, it is possible to compare the value ranges.

The sample *Hydrolytic lignin* is the result of the extraction at the next conditions:

Stage	T (°C)	P (bar)	t (min)
1	90	20	60
2	150	20	20
3	250	80	20
4	320	160	20

Table 10. Extraction conditions of the lignin from subcritical water hydrolysis

At the first stage, the extraction is made by ethanol 75% (v/v). With ethanol, polyphenols and oils are extracted from the sample. The following stages used water for the hydrolysis. At the second hydrolysis, the

hemicellulose is separated. At the third stage, cellulose is extracted and finally, at the last stage, the hydrolytic lignin remains in the reactor. Then, the hydrolytic lignin is dried at 60°C until constant mass.

Extracted grape seeds is a sample result of an extraction of 60 minutes with ethanol, at a temperature of 90°C and a pressure of 20 bar. Once this sample is extracted from the reactor, the grape seeds are dried at 60°C until constant mass.

Typical values of HHV (without humidity) of several biomass materials are listed in Table 11.

Samples	HHV (kJ/g)
Almond shell	19.93
Nut shell	18.84
Peanut	17.79
Cereal straw	18.51
Rice husk	17.29
Vine shoot	19.09
Carton	18.51
Conifer sawdust	20.43

Table 11. HHV of several samples ((IDAE) 1996)

The results obtained without humidity are:

Samples	HHV (kJ/g)
Grape seeds	20.04 ± 0.058
Cellulose	17.35 ± 0.055
Hydrotropic lignin	24.78 ± 0.048
Alkali lignin	28.00 ± 0.041
Hydrolytic lignin	27.86 ± 0.046
Extracted grape seeds	25.30 ± 0.047
Anhydrous Glucose	16.64 ± 0.055

Table 12. HHV of the samples studied

It is shown that lignins have the higher values of HHV. This can be expected since lignin has a very complicated molecular structure.

3.4. Estimating Errors

3.4.1 Calibrations

With several calibrations with benzoic acid, it has been determined:

- the average of the values of the parameter of the system: $(m \cdot cp)_i$,
- the standard deviation of those values, and, finally
- the calibration error, e , that exists in the following form:

$$e = \frac{s}{(m \cdot cp)} \quad (10)$$

Calculating these parameters for two or more standards, we can compare the results and determine if the calibration of the system is right.

Also, if we calculate the same parameters taking into account all the values of (m.cp) of the calibrations, the results are:

	Benzoic Acid	Anhydrous Glucose	Global Calibration
m·cp (kJ/°C)	12.87	12.95	12.91
s (kJ/°C)	0.25	0.44	0.33
	1.9%	3.4%	2.6%

Table 13. Average calibration parameter and standard deviation

3.4.2 Validating calibrations

As discussed above, in Section 2.3.1, there have been several calculations for the temperatures before and after ignition. The results for each sample used, are shown in the summary table below.

Sample	Nº of combustion	T before Ignition (°C)	T after Ignition (°C)	Average T before ignition (°C)	Average T after ignition (°C)
Grape seeds	1	22.41	24.22	22.38	24.20
Grape seeds	2	23.92	25.66	23.91	25.63
Cellulose	1	22.78	24.02	22.76	23.98
Cellulose	2	23.63	24.85	23.62	24.82
Hydrotropic lignin	1	24.42	26.07	24.44	26.06
Hydrotropic lignin	2	25.46	26.92	25.46	26.90
Alkali lignin	1	24.90	26.31	24.89	26.28
Hydrolytic lignin	1	23.51	24.90	23.50	24.89
Extracted grape seeds	1	23.54	25.22	23.55	25.20
Anhydrous Glucose	1	24.61	26.00	23.00	24.23
Anhydrous Glucose	2	21.97	23.20	23.18	24.58

Table 14. Experimental temperatures registered

Sample	N° of combustion	s before (°C)	s after (°C)	average s (°C)	error before (%)	error after (%)	average error (%)
Grape seeds	1	0.017	0.012	0.015	0.076	0.049	0.063
Grape seeds	2	0.012	0.014	0.013	0.050	0.056	0.053
Cellulose	1	0.012	0.013	0.013	0.054	0.054	0.054
Cellulose	2	0.015	0.012	0.014	0.063	0.047	0.055
Hydrotropic lignin	1	0.012	0.009	0.011	0.050	0.033	0.042
Hydrotropic lignin	2	0.011	0.009	0.010	0.043	0.032	0.038
Alkali's lignin	1	0.010	0.011	0.011	0.040	0.041	0.041
Hydrolytic lignin	1	0.012	0.010	0.011	0.052	0.039	0.046
Extracted grape seeds	1	0.012	0.011	0.012	0.050	0.043	0.047
Anhydrous Glucose	1	0.019	0.013	0.016	0.081	0.053	0.067
Anhydrous Glucose	2	0.011	0.010	0.011	0.044	0.043	0.044

Table 15. Standard deviation and error of the experimental data

4. CONCLUSIONS

According to the need of research into renewable energy as an alternative source to current fuels, this work has been developed. After preliminary studies in the literature, it has been shown that biomass is possible biooils generation and energy generation (as a combustible) and, after the combustion performed in the laboratory, it is possible to appreciate that the raw materials, with or without treatment have a greater or lesser extent, combustion heat.

When pellets are made, it has been necessary to agglomerate the sample with benzoic acid or with cellulose. Cellulose is preferred because samples that are burnt are biomass and cellulose is too. However, some of the sample is lost but always maintaining an amount more or less reproducible to be introduced into the bomb for combustion

It is demonstrated that the heat lost during the combustion will be, as maximum, of 6%, without acting in temperature. So, it is feasible rejecting this term in the energy balance.

About the behavior of temperatures in all cases the combustion curve acquires the same way. The study of the variations in the temperatures, before and after ignition, provides that the election of these was successful, showing minimum standard deviations and errors, with different value in each case.

As it is shown, the typical deviation values of the experiments (s) are not significant, on the order of 0.013 °C. This indicates the system is stable, that means that the system have no losses. Once the maximum is reached in the combustion, the temperature drops slowly.

The final HHVs of three types of lignin, alkaline (19.82 kJ/g), hydrotropic (26.54 kJ/g) and from subcritical water hydrolysis (26.19 kJ/g) show that the alkaline lignin is more degraded and less valuable than the extracted lignin types. Cellulose (16.31 kJ/g), anhydrous glucose (15.64 kJ/g), grape seeds (18.84 kJ/g) have similar values. After extracting with ethanol at 90°C the extracted grape seeds (23.78 kJ/g) have a higher HHV.

Calibrations repeatability for a standard of Benzoic Acid was 1.9% and for a standard of Anhydrous Glucose was 3.4%. The calibration parameter of the system corresponds to a value of $m \cdot c_{pi} = 12.91 \text{ kJ/}^\circ\text{C}$, the standard deviation, to a value of $s = 0.33 \text{ kJ/}^\circ\text{C}$, so therefore, the error with it is been working is 2.6%.

5. NOMENCLATURE

T	Temperature (°C)
s	Standard deviation (°C)
e	Error (%)
ΔH	Heat of combustion (kJ/g)
m	Mass (g)
Q	Heat (W)
U	Global coefficient of heat transfer ($W/m^2 \text{ } ^\circ C$)
S	Heat transfer area (m^2)
D	Diameter (m)
L	Length (m)

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