*Full Research Paper*

# Combustion Analysis of Different Olive Residues

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**Abstract:** The Thermogravimetric Analysis (TGA) techniques and concretely the study of the burning profile provide information that can be used to estimate the behaviour of the combustion of carbonous materials. Commonly, these techniques have been used for the study of carbons, but are also interesting for the analysis of biomass wastes, due to the different species present on the wastes affect directly to its thermal properties. In this work, techniques of thermal analysis have been applied to compare the behaviour of different wastes coming from olive oil mills. From these results, it is remarkable that the Concentrated Olive Mill Waste Water (COMWW) presents more unfavourable conditions for its combustion.

**Keywords:** reactivity; biomass; TGA.

## 1. Introduction

Nowadays, the thermochemical processes such as pyrolysis, gasification and combustion are the most attractive and practical as far as the energy recovery from the biomass is concerned [1], being the combustion responsible for about a 97 % of the production of bioenergy in the world [2]. In Spain, the

thermal processes are the option most widely used for the treatment of the waste coming from the industries for the transformation of agricultural products, specially interesting are the wastes from the olive oil mills, owing to the big amount produced and its elevated heating value between 20 kJ/kg and 23 kJ/kg dry basis.

To carry out a correct design of the systems for thermochemical treatment and control them properly, it is important to know deeply the different states and complex transitions that take place in the biomass wastes as the temperature varies [3].

In the case of the biomass, and similarly to the carbon, the reaction rates are influenced by the composition and size of the particle size. Therefore, and both in the operation conditions and in the design procedure of the plant, the knowledge of the reactivity and the combustion kinetics of the fuels gives a valuable information for the combustion system of the fuel [4].

Considering also that the combustion of the biomass waste differs notably from the combustion of the conventional solid fuels, it is evident that the system used optimally for these ones are not suitable for biomass fuels.

Another factor to consider is the heterogeneity existing within the different biomass wastes, which does not allow to generalize when it comes down to the convenience of thermochemical treatment systems and general characteristics and dimensions of the equipment involved.

Therefore, it is essential to carry out a specific thermal analysis of the biomass to be used, in order to predict more accurately how it is going to behave in real systems. The limitations of these methods regarding their generalization have to be taken into account, since they are carried out in controlled laboratory conditions and over small samples in comparison with those ones used in real life.

The Thermogravimetric Analysis (TGA) is one of the main techniques used for the study of the thermal behaviour of carbonous materials and the kinetics of the thermal decomposition reactions of different solid fuels [5-8], etc. The analysis of the characteristics of the combustion allows obtaining the "burning profile" of the fuel, defined as the representation of weight loss versus temperature in an oxidizing atmosphere [9]. From these results the reactivity can be determined as an indicator of the combustion potential of a carbonous material [1], [10]. Other authors [11], [12], indicate that the information obtained from the burning profiles in the TGA in the case of fuels like carbon can be used to estimate the behaviour of the combustion in industrial scale.

In this work, TGA techniques and other characterization tests have been used to evaluate the thermal behaviour in oxidizing atmosphere of different olive wastes, such as olive pit, pulp, residual olive cake and Concentrated Olive Mill Waste Water (COMWW).

The behavior of the wastes has been compared in terms of emissions of nitrogen oxides, soiling phenomenons, corrosion and ash melting problem. Also, it will be shown the thermal behavior of the wastes and its reactivity in an air atmosphere. In addition, the combustion in an industrial plant of the different fractions obtained has been studied in order to assess the viability of this process.

## 2. Materials and Methods

The origin of each of these fractions in the plant is the following one: the two-phases Olive Mill Solid Waste (two phases OMSW) comes from the olive mill and, once in the installation, is firstly processed to extract its pits. Once the olive pit has been separated, the two-phases OMSW is processed

in a three-phases continuous system, obtaining wet olive cake and Olive Mill Waste Water (OMWW). The olive cake is dried in a rotating dryer. Then, the lightest fraction, called pulp, is separated from the dry olive cake by a pneumatic system, remaining another fraction consisted of a smaller waste of olive pit and the most solid part of the pulp, called residual olive cake.

The OMWW is taken to a concentration tower in which the residual heat from the drying process can be used for the reduction of the moisture. The resulting product, COMWW, presents a moisture of around 70 %.

The characterization of the four fractions analyzed has been carried out: heating value, ultimate analysis, proximate analysis, chemical analysis, chemical composition of ashes and ash melting analysis. Calorific values were measured using a Parr 1351 Adiabatic Bomb. C, H, N, S contents in the four fuels were analyzed using a Eurovector EA 3000 Elemental Analyzer and chlorine was determined by the Eschka method. The moisture content of the samples was obtained by drying till constant weight in a HOLELAB Oven. Ash content and volatile matter were determined after slow combustion of the samples in a HOBERSAL HD-230 furnace. Finally, the fixed carbon content was calculated by difference. Cellulose, Hemicellulose and lignin were analyzed acording to standards LAP-002, LAP-003, LAP-010 and LAP-005. Chemical composition of ashes in the four samples was measured using X-ray fluorescence spectrometer Philips PW 2400 under standard conditions and ash melting analysis were carried out in an oxidizing atmosphere by a LECO AF-600. All the analysis were measured according to the normalized methods ASTM.

For the determination of the combustion profiles of the different wastes, dynamic experiments have been done in air atmosphere in a TG/DTA thermal analyzer METER TOLEDO TGA/SDTA 851, with horizontal oven and an only arm. The precision for the TGA is ± 0.1 µg and for the SDTA is 0.005 ºC. The temperature of the oven in the thermobalance is controlled so that the sample follows the desired profile. This device has a temperature precision of ±0.25 ºC.

It is important to remark that in the case of particles smaller than 1mm the chemical reaction controls the process, whilst in the case of bigger particles heat and mass transfer phenomenons [13-16] also take part in the control process. Taking this into account, samples of olive pit, pulp and residual olive cake have been prepared in a centrifuge mill RETSCH ZM 100, choosing a sieve that guarantees a sample granulometry lower than 1mm.

To ensure the uniformity of the temperature in the sample, its size is recommended to be small [5], [17], [18]. However, if the sample is not homogeneous a bigger sample mass is necessary. Samples between 10-30 mg have been chosen in the case of dry waste and 50 mg in the case of the COMWW. To obtain a noiseless signal the gas flow must be uniform. Therefore, a constant gas flow of 100 ml/min is used to feed the system in all the tests.

The different samples are processed by TGA in air atmosphere. The most common range of ramp reported by the literature for TGA characterization of biomass appears to be 10-50 ºC/min [19-22], thus 30 ºC/min was chosen as an average value in order to make this analysis. Samples are heating from ambient temperature to 800 ºC, in order to ensure no significant further changes above this top limit. For each experimental point, the reproducibility was checked by at least a duplicate run.

In all the cases the next parameters are determined: initial temperature, corresponding to the point in which the rate of weight loss is >1%/min after the initial moisture loss peak; maximum temperature, corresponding to the point in which the weight loss rate of the sample due to the combustion is

maximum (maximum combustion rate), and ending temperature corresponding to the point in which the char's combustion is finished (ending temperature was extrapolated from the slope of the combustion profile in a section where calcination had not started yet). Apart from all these parameters mentioned, a detailed analysis of the combustion profile is carried out.

## 3. Results and Discussion

### 3.1. Physical and Chemical Characteristics

Tables 1, 2 and 3 present the results obtained for the four fractions regarding their heating values, ultimate analysis, proximate analysis, chemical analysis, chemical composition of the ashes and their melting temperature.

**Table 1.** Physical and chemical characteristics of olive pit, pulp, residual olive cake and concentrated OMWW.

| | Pit | Pulp | Residual Olive cake | COMWW |
|---|---|---|---|---|
| **Ultimate Analysis (% dry basis)** | | | | |
| Carbon | 52.270 | 55.205 | 54.895 | 50.075 |
| Hydrogen | 7.485 | 7.960 | 8.215 | 7.795 |
| Nitrogen | 0.060 | 1.995 | 2.220 | 2.125 |
| Oxygen | 40.097 | 34.042 | 34.386 | 39.752 |
| Sulfur | <0.1 | <0.1 | <0.1 | <0.1 |
| Chlorine | 0.088 | 0.798 | 0.284 | 0.253 |
| **Proximate Analysis (% dry basis)** | | | | |
| Volatile | 80.94 | 79.10 | 77.77 | 69.29 |
| Ash | 0.56 | 5.60 | 4.31 | 18.82 |
| Fixed Carbon | 18.50 | 15.30 | 17.92 | 11.89 |
| Moisture (% wet basis) | 9-10 | 6-6.5 | 5.5-6 | 70-73 |
| **Chemical Analysis (% dry-extractive free basis)** | | | | |
| Cellulose | 18.6 | 12.1 | 12.4 | 0.6 |
| Hemicellulose | 25.1 | 12.2 | 14.4 | 0.6 |
| Lignin | 39.3 | 43.3 | 42.8 | 51.3 |
| **Higher heating value (MJ/kg, dry basis)** | 20.61 | 23.39 | 22.42 | 21.36 |
| **Higher heating value (MJ/kg, dry-ash free basis)** | 20.70 | 24.35 | 23.27 | 26.29 |
| **Lower heating value (MJ/kg, dry basis)** | 18.96 | 21.64 | 20.61 | 19.64 |

As observed in table 1, the pulp is the by-product with higher heating value (HV), being the olive pit the one with lower HV.

**Table 2.** Ash melting temperatures of olive pit, pulp, residual olive cake and concentrated OMWW.

|  | Pit | Pulp | Residual Olive cake | COMWW |
|---|---|---|---|---|
| **Initial (°C)** | 1165 | 1185 | 1165 | 1040 |
| **Deformation temperature (°C)** | 1320 | 1195 | 1185 | 1050 |
| **Hemisphere temperature (°C)** | 1335 | 1235 | 1195 | 1055 |
| **Flow temperature (°C)** | 1340 | 1350 | 1330 | 1215 |

**Table 3.** Ashes composition of olive pit, pulp, residual olive cake and concentrated OMWW.

|  | $Na_2O$ | $K_2O$ | CaO | MgO | $SiO_2$ | $P_2O_5$ | $Fe_2O_3$ | MnO | TiO | $Al_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **Pit (%)** | 0.95 | 42.88 | 8.44 | 1.51 | 12.98 | 3.43 | 0.91 | 0.05 | 0.07 | 0.90 |
| **Pulp (%)** | 0.38 | 39.61 | 7.52 | 2.04 | 18.51 | 6.22 | 1.37 | 0.04 | 0.11 | 1.95 |
| **R. O. cake (%)** | 0.51 | 34.62 | 8.50 | 1.87 | 24.59 | 5.64 | 1.34 | 0.04 | 0.13 | 2.44 |
| **COMWW (%)** | 0.94 | 57.29 | 2.84 | 2.49 | 1.14 | 7.84 | 0.37 | 0.03 | 0.04 | 0.33 |

From the ultimate analysis, it is remarkable the presence of high percentages of chlorine in all the wastes, except for the case of the olive pit. This fact could produce soiling phenomenons and the formation of dioxins if the combustion temperatures are low. The admissible percentages of chlorine for the proper use of the biomass are: 0.1%, to avoid corrosion problems and emissions of HCl; and 0.3 %, to avoid the formation of dioxins and furans [18]. From the results obtained for the different wastes, and except for the case of the olive pit, all the by-products can present problems of corrosion and emissions during their combustion. However, the formation of dioxins and furans is not expected a priori, since the combustion temperature must be higher than 500 °C in all the cases (see table 4).

The olive pit is also the waste with lower percentage of nitrogen. Therefore, the emissions of oxides from this element will be minimum. For the rest of wastes, the values obtained are around 2 %, being able the formation of oxides from the nitrogen of the fuel. According to Van Loo and Koppejan [23], percentages of nitrogen higher than 0.6 % can cause problems related to the emissions of nitrogen oxides.

Finally, as far as the emissions of $CO_2$ are concerned, though the variations are not very significant, the higher H/C ratio in the COMWW (see figure 1) indicates a lower level of $CO_2$ in the gases per unit energy produced.

Pulp and residual olive cake present a similar chemical composition, showing cellulose and hemicelluloses proportions lower than that found on the olive pits and higher than the value measured on the COMWW. Additionally, the highest amount of lignin can be found on the COMWW, being followed by pulp, residual olive cake and olive pits, respectively. This result confirmed that the ash free basis heating value of the wastes increases along with the lignin proportion on the sample [24].

From the ultimate analysis, it is remarkable the high percentages of moisture and ash in the COMWW. The first value will show the need of using an additional fuel for this by-product or the need of a previous drying process. As for the ash content and its composition, the high presence of

water-soluble metals such as sodium or potassium, favours its accumulation in the OMWW and, later, in the COMWW. This fact affects notably the ash melting [23], as can be observed in the analysis of table 2 and in figure 2, which shows the deformation temperatures, the percentages of ashes and their $K_2O$ content. Literature reports that the increase of $K_2O$ amount on the ashes decreases the melting point [25]. Other elements such as Silicon can decrease either this temperature, appearing on the ashes as $SiO_2$. Despite the melting point of this oxide is around 1450 ºC [26], it can form a eutectics mixture with the K2O showing a lower melting point around 800ºC [27].

Taking into account that the COMWW is also the waste with higher levels of ash, it can be expected that the fusion and ash removal processes for this by-product cause several problems.

**Figure 1.** Hydrogen/Carbon ratio for the olive pit, pulp, residual olive cake and concentrated OMWW.
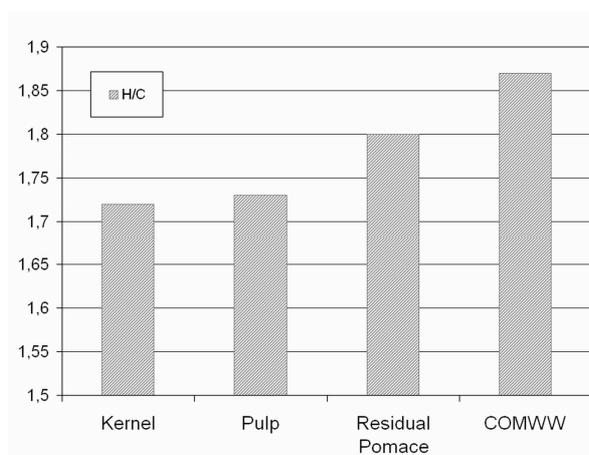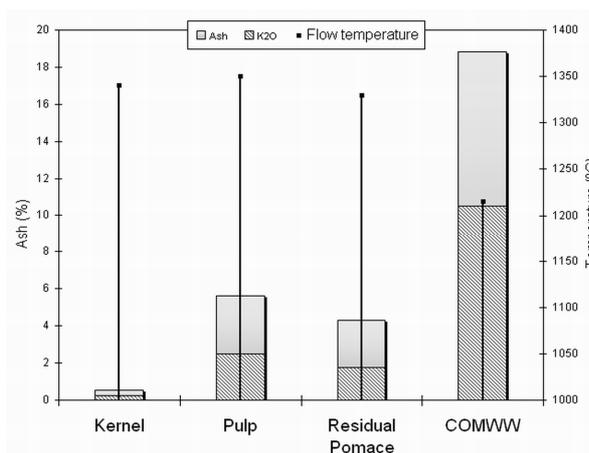


**Figure 2.** Deformation temperature, percentages of ashes and their $K_2O$ content for the wastes analyzed.



*3.2. Thermogravimetric analysis of the olive pit, pulp and residual olive cake.*

Figures 3, 4 and 5 show the weight loss velocity with respect to the temperature in oxidizing atmosphere in the case of the olive pit, the pulp and the residual olive cake.

The first peak observed corresponds to the moisture loss and happens at temperatures between 70 ºC and 90 ºC, depending on the waste. It decreases at temperatures between 125 ºC and 140 ºC.

The olive pit presents the maximum values of weight loss rate corresponding to moisture lost, being the waste with higher percentage of moisture and with the lower ash content (0.56 % dry basis). After the drying process, a mass loss in the sample can come about due to the emission of gases absorbed and the loss of very light volatiles.

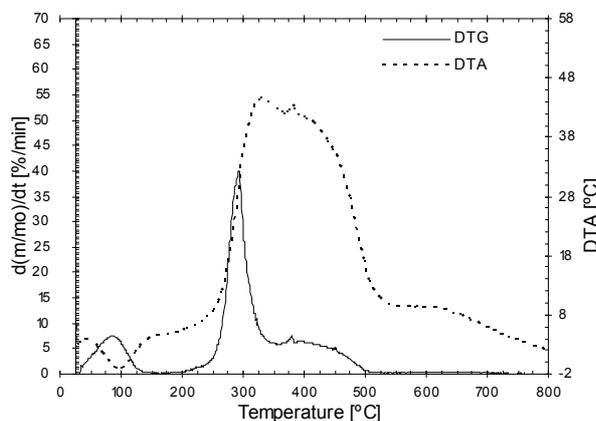**Figure 3.** Olive pit's combustion profile and temperature variation in the sample.



**Figure 4.** Pulp's combustion profile and temperature variation in the sample.
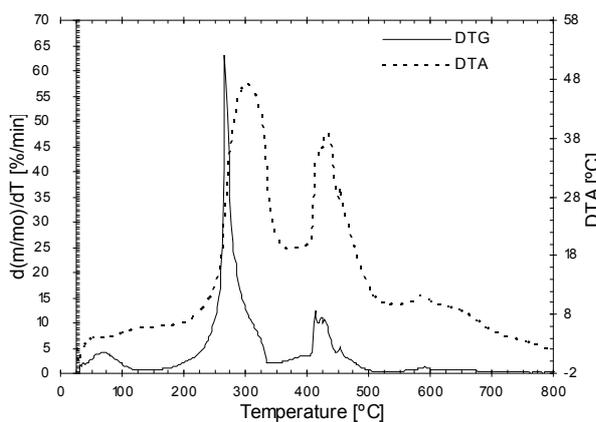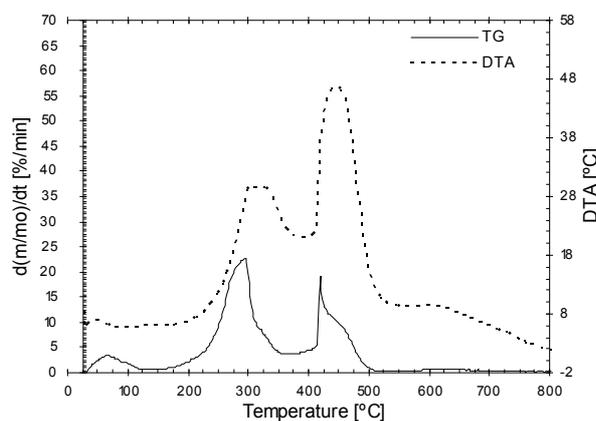


**Figure 5.** Residual olive cake's combustion profile and temperature variation in the sample.

For temperatures between 180 ºC and 200 ºC a sudden mass loss happens in the samples, due to the beginning of the emission of some volatiles and their combustion. In the region of fast combustion the maximum mass loss takes place. The loss velocity becomes slower immediately for temperatures between 300 ºC and 400 ºC for the pulp and the residual olive cake. The olive pit samples present different behaviour compared to the other two samples.

After this point the burning ratio decreases, and after a short period it increases again, more significantly in some wastes than in others, producing continuous mass losses until over 500 ºC due to the oxidation of the char. For higher temperatures, reductions in the mass can occur, which can be attributed to volatile metal loss and carbonate decomposition [28].

However, as can be observed in the DTA curves of figures 3, 4 and 5, the absence of increments in the temperature indicates that the combustion of the char has already concluded before the beginning of this last period.

Table 4 shows the different parameters that characterize the combustion profile of the three solid fractions studied and the COMWW.

The peak and initial temperatures are the most representative ones in the burning profile. The initial temperature is determined from the profile of the samples, obtaining values of 220 ºC, 183 ºC and 181 ºC for the olive pit, the pulp and the residual olive cake, respectively. This shows that the olive pit is the waste that takes longer to react with the temperature, needing an increase of 40 ºC with respect to other wastes.

**Table 4.** Properties of the samples in the combustion process.

|  | Pit | Pulp | Residual Olive Cake | COMWW |
|---|---|---|---|---|
| **Initial temperature (ºC)** | 220 | 183 | 181 | 161 |
| **Maximum combustion rate (%/min)** | 39.82 | 63.01 | 22.81 | 10.27 |
| **Peak temperature (ºC)** | 292 | 267 | 295 | 653 |
| **Burnout temperature (ºC)** | 530 | 509 | 519 | 743 |
| **Rm (% min$^{-1}$K$^{-1}$)** | 7.05 | 11.66 | 4.01 | 1.11 |

Haykiri-Açma [9] presents values of the initial temperature for different biomass wastes, concretely 202ºC for the sunflower shell, 150 ºC for the colza seed, 202 ºC for the pine cone, 150 ºC for the cotton refuse and 200 ºC for the olive refuse. García [29] presents values of the starting temperature between 179 ºC and 193 ºC for different samples of dry OMSW, very close to the ones obtained for the samples analyzed.

The value of the initial temperature for coals with different ranges is between 235 ºC and 441 ºC [30], corresponding the higher values to the carbons with higher carbon percentage in their composition. In the case of the waste studied here this effect does not take place, since the olive pit, the waste with lower carbon content, begins to react at the highest temperature.

In the case of the lignocelluloses material, the temperature of degradation and the thermal degradation rate of the hemicelluloses and lignin are lower than the values that can be found on the cellulose [31]. Therefore, the initial temperature of degradation is higher in the olive pits, which

present a high amount of cellulose in comparison with the pulp, olive cake and COMWW as the literature reports [8]. In addition, it should be pointed out that a fuel with a higher percentage of ashes and impurities in his composition, presents a lower initial temperature of degradation, this effect takes place in the case of the pits, due to a lower amount of ashes on the wastes [32].

As commented previously, the point of the burning profile in which the maximum weight loss comes about due to the combustion is called peak temperature. This point is considered as an indicator of the reactivity of the sample. The peak temperature for the different samples are 292 ºC, 267 ºC and 295 ºC for the olive pit, the pulp and the residual olive cake, respectively. The pulp is the waste with higher value of $DTG_{max}$ (63.01% min$^{-1}$) followed by the olive pit (39.82 % min$^{-1}$) and finally by the residual olive cake (22.81 % min$^{-1}$). From the results corresponding to the analysis of the samples, it is observed that the olive cake is the waste with lower initial temperature and the pulp is the waste with higher maximum weight loss velocity.

Haykiri-Açma [9] determines the values for the maximum combustion velocity of different biomass wastes, that is, 5.5 mg min$^{-1}$ for the sunflower shell, 2.8mg min$^{-1}$ for the colza seed, 5.2 mg min$^{-1}$ for the pine cone, 3.7 mg min$^{-1}$ for the cotton refuse and 3.4 mg min$^{-1}$ for the olive refuse, being the initial mass of the sample 40 mg. In all the cases, Haykiri-Açma [9] obtains much lower values than those obtained in our study.

García [29] determines the maximum burning velocity of two samples of dry OMSW for three different heating ramps. With a ramp of 20 ºC min$^{-1}$, values of 2.6 mg min$^{-1}$ and 4.3 mg min$^{-1}$ are obtained for samples with an initial weight of 10 mg, approximately. These values are close to the ones obtained for the olive pit and the residual olive cake, being lower than the ones obtained when the pulp sample gets oxidized.

As far as the conventional solid fuels are concerned, Benfell et al. [33] obtained maximum burning velocities between 25 % min$^{-1}$ and 31 % min$^{-1}$ for different types of carbon with a heating ramp of 15 ºC min$^{-1}$ and samples of 5 mg, approximately. This fact shows the higher reactivity of the olive pit, pulp and residual olive cake in comparison with the carbon.

Taking into account that the reactivity of a fuel can be considered directly proportional to its maximum weight loss velocity and inversely proportional to the value of temperature for which it happens [34], it is interesting to introduce a parameter relating both magnitudes [35] and giving an average value of the reactivity of the fuel. This parameter can be defined according to equation (1) and represents the weight loss per unit temperature.

$$R_m = 100 \cdot DTG_{Tp} \cdot T_p^{-1} \ (\% \text{min}^{-1}\text{K}^{-1})$$

(1)

The values obtained for each one of the fuels are presented in table 4. This factor confirms that the waste with better combustion properties is the pulp, followed by the olive pit and finally by the residual olive cake.

Another important parameter to consider is the burning temperature, which allows to obtain a qualitative information regarding the necessary residence time of the fuel that minimizes the unburnts. Carpenter [36] shows that, in the case of the carbon and from the TGA results, the residence time of the fuel in a large scale installation can be estimated. If the sample has a low value of the burning temperature, the presence of unburnts is reduced, whilst samples with higher values of this temperature

are more difficult to burn and will need higher residence times and higher temperatures for their complete combustion.

It is necessary to take into account that TGA and DTG curves, compared with the real combustion, present lower heating velocity and, therefore, the emission of volatiles happens at a lower temperature. According to Su et al. [37], this fact reduces both the amount of volatile matter that can react with the fuel and the burning potential. This way, the results obtained from the TGA will show poorer burning conditions than the ones in a real plant.

In the case of the waste analyzed, the burning temperatures obtained are 530 ºC, 509 ºC, and 519 ºC for the olive pit, the pulp and the residual olive cake, respectively. These values are close to each other but slightly lower than in the case of the pulp, which indicates that the residence time of this fuel will be predictably shorter than in the case of the other wastes. In all the cases burning temperatures lower than those for the fossil fuels are obtained. Alonso et al. [30] present values between 530 ºC and 810 ºC for the coal of low-high rank in tests carried out with a ramp of 25ºC min$^{-1}$.

## 3.3. Thermogravimetric analysis of the COMWW.

To study the thermal behaviour of the COMWW, a first test has been carried out in which an original sample with moisture of 73 % is processed by a heating program of 30 ºC/min. The presence of a big amount of water impedes the analysis of the data obtained, since the moisture loss takes place until high temperatures, hiding the degradation reactions and producing an important thermal demand.

For that reason a previous drying program in the thermobalance has been carried out, long enough to guarantee the total dryness of the sample, minimizing the possibility of liberation of other products. This way, it is determined that this objective is fulfilled with a previous heating of the sample during 35 min at 100 ºC and followed by a ramp of 30 ºC/min. The results obtained from this test are presented in figure 6.

**Figure 6.** Concentrated OMWW's combustion profile and temperature variation of the sample.
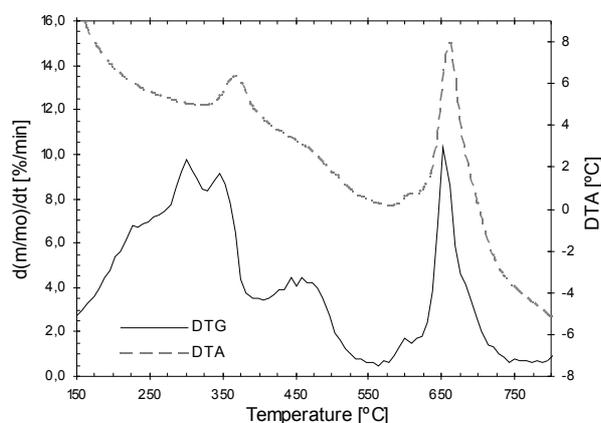


As can be observed, the mass loss begins when the temperature of the sample increases over 150ºC, due to the beginning of the liberation of some volatiles and their combustion. In the fast combustion region, a maximum of mass loss occurs. The mass loss velocity becomes lower immediately at

temperatures close to 350ºC and increases slightly, again, between 400ºC and 500ºC. Alter that point, the burning ratio decreases and, after a short period it increases significantly, obtaining the maximum value of the burning velocity due to the oxidation of the char.

Table 4 shows the different parameters that characterize the combustion profile of the COMWW.

The sample presents an initial temperature of 161 ºC, lower than the one obtained for el olive pit, the pulp and the residual olive cake, with values of 220 ºC, 183 ºC, and 181 ºC, respectively.

The peak temperature, temperature with the maximum burning velocity, has a value of 653 ºC, much higher than for the rest of wastes, with values of 267-295 ºC for the solid olive residues. This temperature takes place in combustion zone of the char, not in the volatiles liberation zone, as happens in the case of the solid wastes.

The COMWW presents a $DTG_{max}$ value of 10.27 % $min^{-1}$, being the velocity for the residual olive cake two times this value, three times higher for the olive pit and more than six times higher in the case of the pulp. The values obtained for this parameter confirms the lower reactivity of this by-product in comparison with the solid wastes. The average value of reactivity for this waste is 1.11% $min^{-1}K^{-1}$, being 7.05 % $min^{-1}K^{-1}$, 11.66 % $min^{-1}K^{-1}$ and 4.01 % $min^{-1}K^{-1}$ for the olive pit, the pulp and the residual olive cake, respectively.

Finally, as far as the burning temperature is concerned, it is important to remark the high value of this parameter in the case of the COMWW, 743 ºC, much higher than those obtained in the case of the solid wastes, 507 ºC, 503 ºC, and 475 ºC, for the olive pit, the pulp and the residual olive cake, respectively. This effect can be due to the highest amount of lignin presents on the COMWW, that increases the char yield and consequently the residence time [38], and to the percentage and composition of the ashes. Rubiera et al. [39] and Vamvuka et al. [40] showed that the demineralised samples presented lower burnout temperatures than those of the parent fuels. Therefore, the residence time of this by-product in the combustion chamber has to be longer than in the case of the solid wastes and the temperatures for the complete combustion has to be higher [36].

## 4. Conclusions

According to the results obtained and the analysis of the characterization of the wastes, it can be concluded that:

The high moisture of the COMWW (around 73%) makes it inviable to keep the combustion process, being necessary the use of an additional fuel.

The percentage of carbon in all the fractions studied is within the normal range for biomass wastes. As for the nitrogen, chlorine, sodium and potassium contents, the values obtained show that, except for the case of the olive pit, problems related to the emissions nitrogen oxides, corrosion and soiling are likely to appear.

As far as the behaviour of the ashes is concerned, the COMWW is the most problematic fraction, since it presents higher amounts of ashes and lower melting point.

Moreover, taking into account the different combustion profiles of the wastes, it can be concluded that:

In the case of the COMWW, the highest mass loss velocity takes place in the combustion zone of the char, instead of in the volatiles liberation zone, which indicates that the combustion of the

COMWW will be slower than in the case of the other wastes, being also necessary a proper amount of air for the combustion of the char formed.

The burning temperatures obtained for the solid fractions are similar to each other. For the COMWW, the burning temperature increases considerably, liberating the most significant amount of heat in the last period of reaction. Therefore, it will be necessary to guarantee appropriate values of temperature and residence times in order to take advantage of its heating value.

The reactivity parameters determined show that the waste with better combustion properties is the pulp, followed by the olive pit, the residual olive cake and finally, with much lower index, by the COMWW. Considering the Rm parameter as an average value of the reactivity, it can be confirmed that the solid wastes present a Rm parameter about 4 to 10 times higher than the value observed on the COMWW.

## Acknowledgements

## References and Notes

1. Leung, D.; Wang, C. Kinetic study of scrap tyre pyrolysis and combustion. *Journal of Analytical and Applied Pyrolysis* **1998**, *45,* 153-169.
2. Demirbas, A. Combustion characteristics of different biomass fuels. *Progress in Energy and Combustion Science* **2004**, *30*, 219-230.
3. Helsen, L.; Van den Bulck, E. Kinetics of the low-temperature pyrolysis of chromated copper arsenate-treated wood. *Journal of Analytical and Applied Pyrolysis* **2000**, *53,* 51-79.
4. Vamvuka, D.; Kastanaki, E.; Lasithiotakis, M.; Papanicolaou, C. Combustion behaviour of xylite/lignite mixtures. *Carbon* **2004**, *42*, 351-359.
5. Ergüdenler, A.; Ghaly, A. Determination of reaction kinetics of wheat straw using thermogravimetric analysis. *Applied Biochemistry and Biotechnology* **1992**, *34-35*(1), 75-91.
6. Bining, A.; Jenkins, B. *Thermochemical reaction kinetics for rice straw from an aproximate integral technique*, ASAE, St. Joseph, Michigan, Tech. Rep. 92-6029, 1992.
7. Antal, M., Jr.; Varhegyi, G. Cellulose pyrolysis kinetics: the current state of knowledge. *Industrial and Engineering Chemistry Research* **1995**, *34*(3), 703-717.
8. Nassar, M. Kinetic studies on thermal degradation on nonwood plants. *Wood and Fiber Science* **1985**, *17*(2), 266-273.
9. Haykiri-Açma, H. Combustion Characteristic of different biomass materials. *Energy Conversion Management* **2003**, *44*, 155-162.
10. Russell, N.; Beeley, T.; Man, C.; Gibbins, J.; Williamson, J. Development of TG measurements of intrinsic char combustion reactivity for industrial and research purposes. *Fuel Processing Technology* **1998**, *57*, 113-130.
11. Cumming, J.W.; McLaughlin, J. The termogravimetric behaviour of coal. *Themochemical Acta* **1982**, *87,* 253-272.

12. Smith, S.E.; Neavel, R.C.; Hippo, E.J.; Miller, R.N. DTGA combustion of coals in the Exxon coal library. *Fuel* **1981**, *60*, 458-462.

13. Antal, J.; Friedman, H.L.; Rogers, F. Kinetics of cellulose pyrolysis in nitrogen and steam. *Combustion Science and Technology* **1980**, *21*(2), 141-149.

14. Conesa, J.; Font, R.; Fullana, A.; Caballero, J. Kinetic model for the combustion of tyre wastes. *Fuel* **1998**, *77*(13), 1469-1475.

15. Williams, P.; Besler, S. Thermogravimetric analysis of the components of biomass. In *Advances in Thermochemical Biomass Conversion*; Blaxkie Academic : London, UK, 1994; pp. 771-783.

16. Caballero, J.; Font, R.; Marcilla, A. Comparative study of the pyrolysis of almond shells and their fractions, holocellulose and lignin. Product yields and kinetics. *Termochimica Acta* **1996***, 276,* 57-77.

17. Wendlandt, W.W. *Thermal methods of analysis*, 2nd Ed; John Wiley Sons: New York, USA, 1974.

18. Ghaly, A.; Ergüdenler, A. Determination of the kinetic of barley straw using thermogravimetric analysis. *Journal of Applied Biochemistry and Biotechnology* **1994**, *45-46*(1), 35-50.

19. Maiti, S.; Purakayastha, S.; Ghosh, B. Thermal characterization of mustard straw and stalk in nitrogen at different heating rates. *Fuel* **2007**, *86*, 1513-1518.

20. Lester, E.; Gong, M.; Thompson, A. A method for source apportionment in biomass/coal blends using thermogravimetric analysis. *Anal. Appl. Pyrolysis* **2007**, *80*, 111-117.

21. García Ibañez, P.; Sánchez, M.; Cabanillas, A. Thermogravimetric analysis of olive-oil residue in air atmosphere. *Fuel Processing Technology* **2006**, *87*, 103-107

22 Lapuerta, M.; Hernández, J.J.; Rodríguez, J. Kinetics of devolatilisation of forestry wastes from thermogravimetric analysis. *Biomass and Bioenergy* **2004**, *27*(4), 385-391.

23. Van Loo, S.; Koppejan, J. *Handbook of Biomass Combustion and Cofiring*, Twente University Press: Enschede, The Netherlands, 2003.

24. Demirbas, A. Relationships between lignin contents and heating values of biomass. *Energy Conversion and Management* **2001**, *42*, 183-188.

25. Department of the Army, *Solid waste incineration*, U.S. Army Corps of Engineers, Tech. Rep., 1998.

26. Wilen, C.; Stahlberg, P.; Sipila, K.; Ahokas, J. In *Energy from biomass and wastes*; Elsevier Applied Science: London, UK, 1987; Chapter: Pelletization and combustion of straw, pp. 469-83.

27. Obernberger, I. Decentralized biomass combustion: state of the art and future development. *Biomass and Bioenergy* **1998**, *14*(1), 33-56.

28 Ross, A.B.; Jones, J.M.; Kubacki, M.L.; Bridgeman, T. Classification of macroalgae as fuel and its thermochemical behaviour. *Bioresource Technology* **2008** (in press).

29. García Ibáñez, P. Estudio del tratamiento de orujillo de aceituna mediante el proceso de gasificación en un reactor de lecho fluidizado. Ph.D. Thesis, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 2004.

30. Alonso, M.; Borrego, A.; Alvarez, D.; Kalkreuth, W.; Menédez, R. Physicochemical transformations of coal particles during pyrolysis and combustion. *Fuel* **2001***, 80,* 1857-1870.

31. Milne, T. *Biomass gasification principles and technology*; Noyes Data Corporation: New Jersey, USA, 1981; pp. 91-118.

32.  Huang, M.; Li, X. Thermal degradation cellulose and cellulose esters. *Journal of Polymer Science* **1998***, 68*, 293-304.

33.  Benfell, K.; Beamish, B.; Rodgers, K. Aspects of combustion behaviour of coals from some New Aeland lignite-coal regions determined by thermogravimetry. *Thermochemical Acta* **1997**, *297*, 79-84.

34.  Ghetti, P.; Ricca, L.; Angelini, L. Thermal analysis of biomass and corresponding pyrolysis products. *Fuel* **1996**, *75*, 565-573.

35.  Zheng, G.; Kozinski, J. Thermal events occurring during the combustion of biomass residue. *Fuel* **2000**, *79*, 181-192.

36.  Carpenter, A.M. *Coal blending for power stations*; IEA Coal Research, Tech. Rep. IEA/81, 1995.

37.  Su, S.; Pohl, J.H.; Holcombe, D.; Hart, J. Techniques to determine ignition, flame stability and burnout of blended coals in P.F. power station boilers. *Progress in Energy and Combustion Science* **2001**, *27*, 75-98.

38.  Rhéna, C.; Öhmanb, M.; Grefa, R.; Wästerlunda, I. Effect of raw material composition in woody biomass pellets on combustion characteristics. *Biomass and Bioenergy* **2007,** *31*, 66-72.

39.  Rubiera, F.; Arenillas, A.; Pevida, C.; García, R.; Pis, J.J.; Steel, K.M.; Patrick, J.W. Coal structure and reactivity changes induced by chemical demineralisation. *Fuel Processing Technology* **2002**, *79*, 273-279.

40.  Vamvuka, D.; Troulinos, S.; Kastanaki, E. The effect of mineral matter on the physical and chemical activation of low rank coal and biomass materials. *Fuel* **2006**, *85*, 1763-1771.