Experiments on torrefaction of *Dichrostachys cinerea* wood: Two Level Factorial Design and thermogravimetric analysis.

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Abstract

The aim of this study is to determine the effect of the temperature and reaction time variables on the solid yield, increment of heating value and composition of the torrefied *Dichrostachys cinerea* wood by using the factorial experiment design and thermogravimetric analysis. The significant factors were identified by means of a Two Level Factorial Design (TLFD) type (2^2), for which the statistical software Design Expert Version 10 was used. Torrefaction and thermogravimetric experimental runs were carried out in a fixed-bed reactor and thermobalance TGA-DTA, respectively. Torrefaction temperature, residence time and their interaction have a significant effect on solid yield. Whilst, the effect of the temperature was the only statistically significant factor on increment at a high heating value (HHV). The R-Squared values for both response variables were greater than 95% in each case. An increase in torrefied biomass was achieved at HHV's of 14.92% and 30.31% to the conditions of 120 min to 250ºC and 290 ºC, respectively. Thermogravimetric characterization and DTG – TG curves of

the torrefied material suggest that the pre-treated material has been modified chemically and structurally.

1. Introduction

In the search for renewable energy sources, energy from biomass is considered a viable choice. The main interest in using biomass as a renewable energy source is within the field of climate change. It is generally accepted that biomass is carbon neutral, provides energy security and can be a resource that is generated locally. The unique position of biomass, as the only renewable source that is a sustainable carbon carrier, makes biomass an attractive energy source (Bridgwater 2012). Biomass is available in a wide range of resources such as waste streams, woody and grassy materials and energy crops (Van der Stelt, Gerhauser et al. 2011). Woody biomass is preferred over food crops, because of many reasons, from energy-related to social factors. Lignocellulosic materials contain much more energy than food crops, the amount of fertilisers and pesticides necessary for wood is much lower and the production of woody materials is much higher than for food crops which means that the amount of land used is lower (Van der Stelt, Gerhauser et al. 2011).

Energy from biomass is based on short-rotation forestry and energy crops that can contribute to the energy needs of contemporary society (Bridgwater 2003, Kaygusuz 2009). During the last few decades, various studies have been published that propose different woody species for use as energy crops, such as: Eucalyptus (*Eucalyptus spp.),* Pine (*Pinus pinea, Pinus halepensis, Pinus brutia, Pinus pinaster*), Poplar (*Populus spp.*), Willow (*Salix spp.)* and Marabu (*Dichrostachys cinerea), (Pérez,*

Renedo et al. , Pereira 1988, Bridgeman, Jones et al. 2008, Abreu, Foppa et al. 2010, Fernández, García-Albalá et al. 2015).

This study will focus on the last species *(Dichrostachys cinerea) as it* has great potential as an energy crop because it is a type of perennial crop that does not require annual reseeding or agricultural inputs (e.g., fertiliser and pesticides). Because of its rapid spread in Cuba, it is estimated that there are approximately 1.2 million ha covered by this invasive plant (Carmenate Germán, Pérez Montesbravo et al. 2008, Pedroso and Kaltschmitt 2012). From the viewpoint of energy, this means a theoretical potential of 700 x 10 GJ. The elemental and proximate analysis, as well as the main characteristics of *D. cinerea* devolatilisation were previously determined and discussed by Abreu, Foppa et al. (2010). The authors demonstrated that this biomass possesses the appropriate characteristics to be used as an energy source: it has a caloric value that is higher than or equal to 19,100 kJ kg^{-1}, 3.4% of ashes and a melting temperature of 1,460ºC, as well as low contents of chlorine and sulphur. Moreover, they determined the main devolatilisation parameters (percentage weight loss, temperatures and degradations rates) and compared it to other lignocellulosic materials, such as corn stover and sugarcane bagasse. Similar results were obtained by Pedroso and Kaltschmitt (2012). This study concluded that *D. cinerea* wood can be used as a promising solid biofuel. The authors compared the *D. cinerea* properties with other types of biomass: Sugarcane bagasse, Germany beech, poplar, wheat straw and rice straw. In addition, they found that the combustion of this species releases low emissions. A simultaneous modelling of pyrolysis and combustion processes of *D. cinerea* and the determination of the kinetic parameters by means of thermogravimetric analysis was investigate by Abreu, Conesa et al. (2012). In a recent study, the opportunities of producing electricity from biomass in the sugar industry were investigated in Cienfuegos, Cuba. The authors

arrived at the conclusion that the *D. cinerea* represents the first potential biomass source followed by sugar cane bagasse. Three scenarios were considered to extend electricity generation from biomass in sugar factories beyond the sugarcane milling season (Sagastume Gutiérrez, Cabello Eras et al. 2016). However, the use of torrefied material from *D. Cinerea* not was assessed as a solid fuel.

Also, the use of this biomass as a raw material for the production of activated carbon or bioethanol has also been studied (Soudham 2009, Villegas and Prieto 2009). However, an analysis of the torrefaction and variations in the main properties of untreated and treated *D. cinerea* wood has not been found in literature.

Biomass can be transformed into energy mainly via physical, thermochemical and biochemical processes. Amongst the various thermochemical conversion methods, gasification is the most promising (Van der Stelt, Gerhauser et al. 2011). In the utilisation of lignocellulosic materials like biofuel, there is a clear need to upgrade some of their properties.

Woody material presents a low energy density value, high moisture content and often the amounts of energy used to obtain small size particles are not inconsiderable. Wood and other biomass can be treated as different ways to provide better properties like fuel material (Prins, Ptasinski et al. 2006).

In this way, torrefaction is gaining attention as an important pre-processing step to improve the quality of biomass in terms of physical properties and chemical composition (Rousset, Macedo et al. 2012). Torrefaction is a thermal decomposition process characterised for its low heating rate, inert atmosphere and a range of temperatures between 200 to 300°C. The aim of the biomass torrefaction is to get a solid homogeneous product with hydrophobic properties and a higher energy density than untreated material. Most of the smoke-producing compounds and other volatiles

are removed during torrefaction, which produces a final product that will have a lower mass but a higher heating value (Jaya Shankar, Christopher et al. 2011). Various studies on the torrefaction of different types of biomass have been published such as: wheat straw (Mei, Che et al. 2016), olive stones (Sánchez and San Miguel 2016) and forest residues (spruce and birch) (Bach, Chen et al. 2016). Nevertheless, a study about the *D. cinerea* torrefaction as a biofuel was not found in the revised literature.

The aim of this study was to contribute to knowledge about biomass in order to obtain a better application of the biomass obtained from *D. cinerea* as a fuel. It was also to determine the effect of the temperature and reaction time variables on the solid yield, increment of high heating and composition of the torrefied *D. cinerea* through the factorial experiment design and thermogravimetric analysis.

2. Materials and methods

2.1. Chemical-physic characterisation

The raw biomass samples used in this study originated in the central region of Cuba. For the preparation of the *D. cinerea* samples, the norms of the European Committee for Standardization (CEN/TS 14780) were used.

The chemical-physical characterisation of the *D. cinerea* had been previously analysed (Abreu, Foppa et al. 2010). The elemental analysis of torrefied wood was determined in accordance to the standard CEN/TS 15104. The equipment model PerkinElmer 2400 CHNO/S of the Biomass Laboratory of Agricultural, Food and Environmental Sciences Department of Polytechnic University of Marche (UNIVPM) was used. The determination of the high heating value (HHV) was carried out in a calorimetric bomb (IKA WERKER KV 500) and the standard CEN/TS 14918.

2.2. Torrefaction experiments in a pilot plant reactor

2.2.1. Torrefaction experimental procedure

It is possible to investigate a number of variables and their effects using a factorial or screening design. The significant factors which affected the response were identified by means of a Two Level Factorial Design (TLFD) type (2^2), for which the statistical software Design Expert Version 10.0.2 (Stat Ease, USA) was selected, as well as ANOVA for the analysis of the results. Design Expert randomizes the performance order of the design of experiments, which contributes to guaranteeing that the model meets some statistical assumptions and can also contribute to reducing the effects of factors not included in the study. As independent variables, the temperature and residence time were selected; and as dependent variables, the percentage of torrefied solid yield and increment in high heating value (HHV) were calculated as follows:

$$increment\ in\ HHV = \frac{HHV_{tor} - HHV_{raw}}{HHV_{raw}} * 100 \hspace{2cm} (eq.\ 1)$$

HHV_{raw} and HHV_{tor} are the high heating values before and after the torrefaction process, respectively.

The level of the two factors (low and high) in coded and uncoded independent variables is shown below in Table 1.

Table 1. The level of variables chosen for the TLFD

Independent Variable	Uncoded and coded variable level		
	Symbol	Low	High
		-1	1
Torrefaction temperature (ᵒC)	A	250	290
Residence time (min)	B	60	120

2.1.2. Description of equipment

The torrefaction experiments were performed in the laboratory of the Department of Chemical Engineering of the University of Alicante, Spain. This reactor was used in

previous thermo-decomposition research (Conesa, Martín-Gullón et al. 2004). A scheme of the reactor system is represented in fig. 1. The system is made up of five main zones.
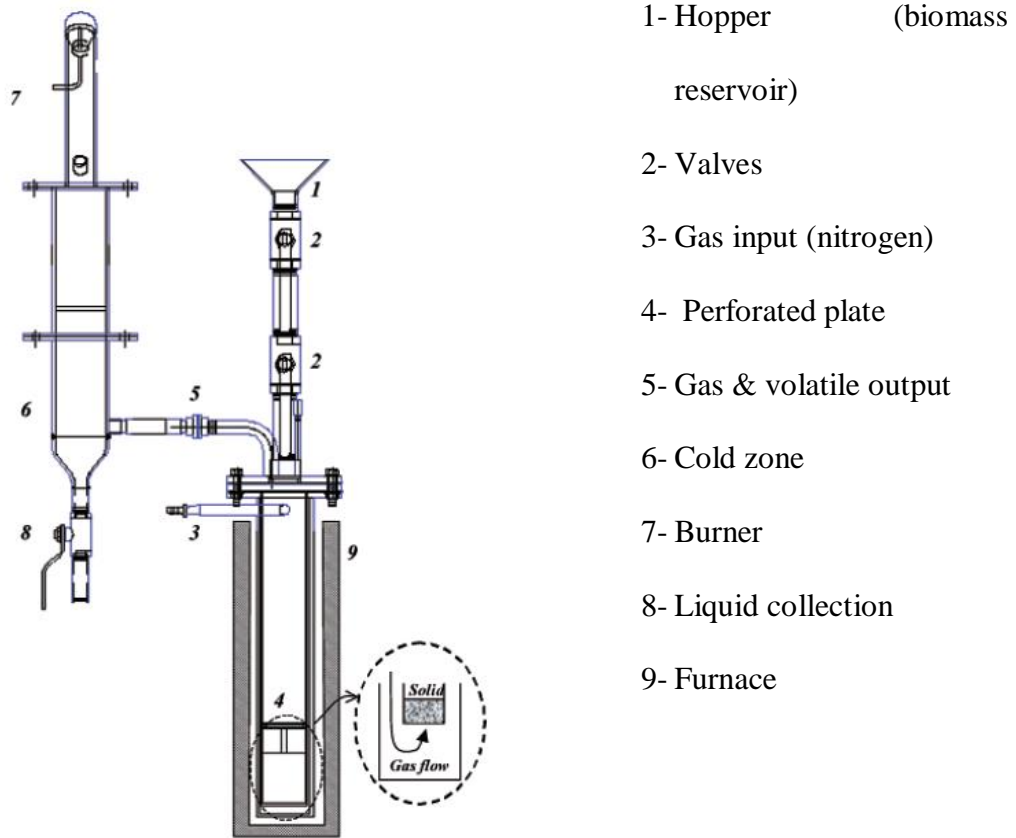

1- Hopper (biomass reservoir)

2- Valves

3- Gas input (nitrogen)

4- Perforated plate

5- Gas & volatile output

6- Cold zone

7- Burner

8- Liquid collection

9- Furnace

Fig. 1. Schematic of the reactor system.

Approximately 40g of biomass are fed to the reactor by a two-valve manual system. The amount of biomass is placed in the hopper and first passes through the upper valve and, after closing it, the lower valve is opened and it passes into the reaction zone. The carrier gas is first preheated by circulating vertically. The gas flow rate was 1.5 L min^{-1}. In the experimental runs, industrial nitrogen (purity = 99.5%) was used.

The temperature is controlled by a type-K thermocouple situated in the furnace and inside the reactor. The measurements at different positions show a maximum difference of 10 °C between the furnace and the inner part of the reactor.

2.2. Thermogravimetric analysis of the torrefied samples

TG runs were carried out in a TGA-DTA (STA PT – 1600) instrument, in which a sample of approximately 12 mg of torrefied material was used with a heating rate of 10 °C min^{-1} from room temperature up to 750 °C in a nitrogen atmosphere. The gas flow rate was 150 mL min^{-1}. The nitrogen was purged for 20 min, before starting the heat programme in order to establish an inert environment.

The main thermogravimetric parameters were determined by means of the methodology suggested by Gronli, Várhegyi et al. 2002, who state:

"T_{onset} temperature [ìs] calculated from the extrapolation of the partial peak of the decomposition of the hemicellulose, which marks the beginning of the active zone of thermodecomosition."

$(dw/dT)_{peak}$ and T_{peak} are the maximum overall decomposition rates, mainly associated to the cellulose decomposition and their corresponding temperature, respectively.

T_{offset} is the extrapolated temperature of the (dw/dT) curve. This value marks the end of the cellulose decomposition.

w_{peak} and $w_{700ºC}$ are weight fractions expressed in percentages at the temperatures of Tpeak and 700 ºC, respectively.

3. Results and discussion

3.1. Torrefaction experiments in pilot plant reactor

3.1.1. Factors affecting bio-oil yield

The effect of the studied factors on solid yield and increment in HHV can be observed in fig 2. The significant effects fall to the right on this plot. Starting on the right we see the largest effects. Temperature, residence time and their interaction have a significant effect on solid yield (Fig. 3a), with "p-value" < 0.05. On the other hand, the effect of

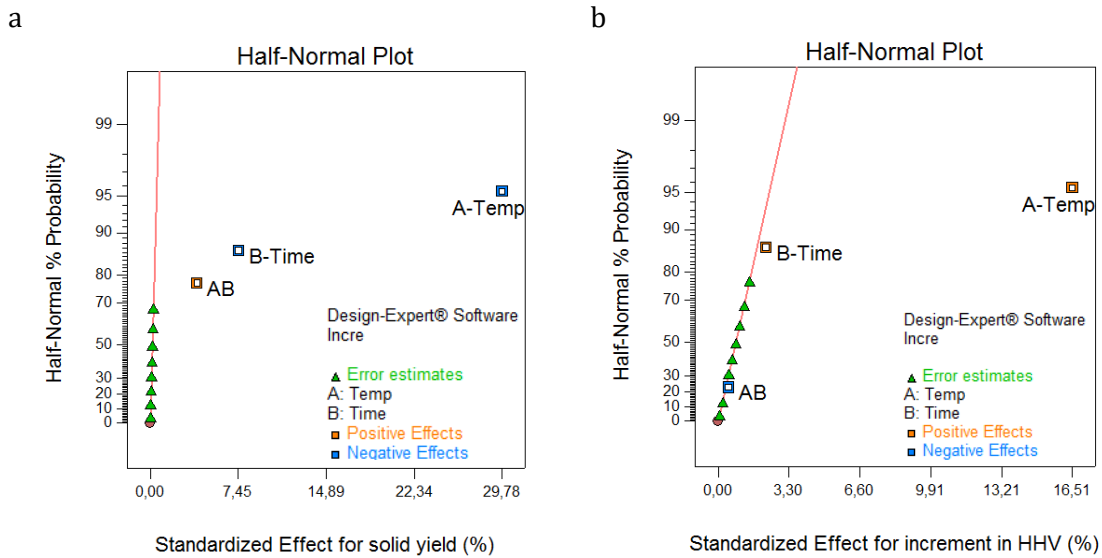the temperature was the only statistically significant factor on increment in HHV (Fig.3b).

Fig. 2. Half normal vs. effect plots for solid yield (a) and increment in HHV (b).

The coded equation is useful in quantifying the relative impact of the significant factors by comparing the factor coefficients (eq. 1 and 2):

$$Solid\ yield = 69.07 - 14.89A - 3.75B + 1.99AB \qquad (eq.\ 2)$$

$$Increment\ in\ HHV = 19.25 + 8.26A + 1.12B - 0.24AB \qquad (eq.\ 3)$$

The R-squared value provided a measure of how much of the variability in the observed response values could be explained by the experimental factors and their interactions. For most studies values above 0.9 are considered a good model. This explains most of the variation in the response (Anderson and Whitcomb 2015). The R-Squared values for both response factors are shown in Table 2 with a high fit, greater than 95% in each case. The difference between the "Pre R-Squared" and "Adj R-Squared" values is in

reasonable agreement, smaller than 0.2 as suggested by Anderson and Whitcomb (2015).

Table 2. ANOVA adjustment coefficient for yield and increment in HHV

	Solid Yield	Increment in HHV
R-Squared	0.9994	0.959
Adj R-Squared	0.9991	0.9437
Pred R-Squared	0.9986	0.9078
Adeq Precision	135.91	15.39

The coded model (eq. 2 and 3) was used to generate surface plots (Fig. 3) for the analysis of the variable effects on solid yield and increment in HHV. The interaction of the studied factors on the dependent variables can be observed in the 3D surface graphs.
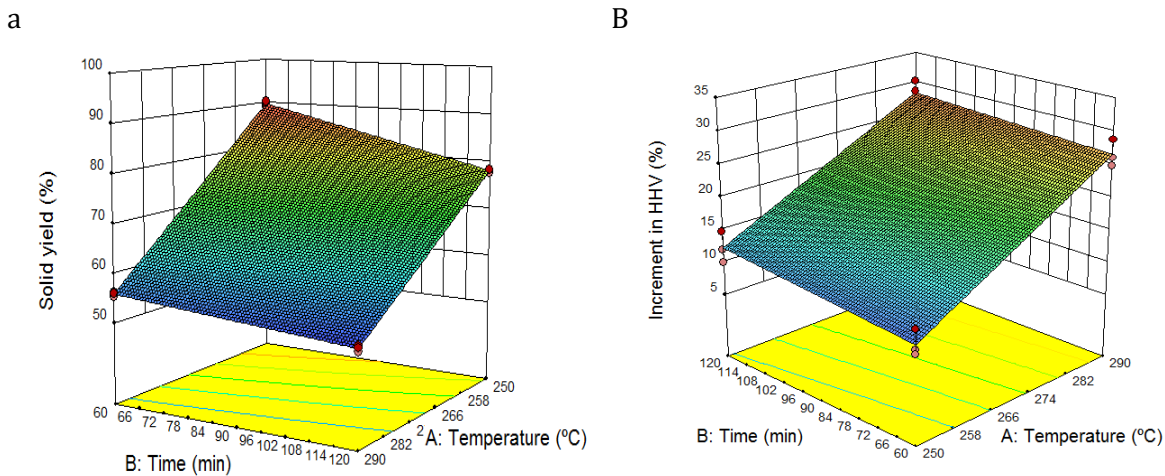
a

B

Fig. 3. 3D Surface plots of Residence Time and Temperature Interaction for the response variables Solid yield (a) and Increment in HHV (b).

As can be seen, in both response factors, the temperature had an effect higher than the residence time. Obviously, the solid percentage decreased with a rise in torrefaction temperature. For torrefaction of lignocellulosic materials, this behaviour is attributed mainly to the decomposition of hemicellulose (Uemura, Matsumoto et al. 2015). On the

other hand, for torrefied biomass an increment in HHV of 14.92% and 30.31% was achieved to the conditions of 120 min to 250 °C and 290 °C, respectively.

Decrease in the solid yield involves an increase in carbon content in the torrefied biomass, whereby an increase in the calorific value occurs. To explain this point, a chart of HHV vs. solid yield was created as shown in Fig. 4. These two variables show a good linear relationship with R-squared equal to 0.92.
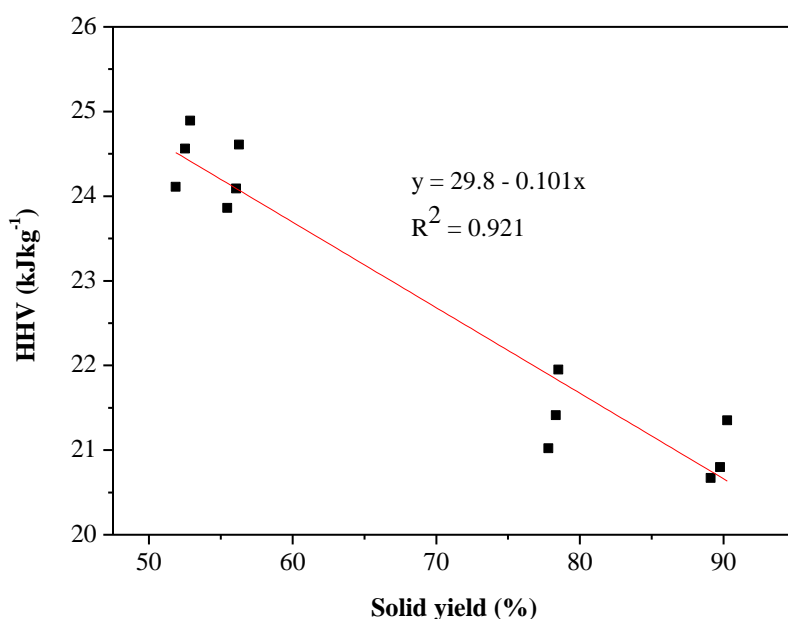

Fig. 4. HHV vs. Solid yield.

3.2. Chemical-physic characterization of torrefied biomass

In order to characterise the torrefied material obtained and be able to compare the values with the untreated material, the elemental analysis of the samples was determined. Table 3 shows the values.

Table 3. Elemental analysis of the *D. cinerea* and torrefied material

Samples	C	H	N	O
	(%) daf			
*D. cinerea**	51.16	6.34	0.82	41.69
250(60)	56.41	6.71	1.74	35.14
250(120)	55.57	6.38	1.70	36.36

290(60)	66.09	6.09	2.04	25.78
290(120)	67.51	5.69	2.02	24.79

Note: **daf** (dry ash free basis). [*](Abreu, Foppa et al. 2010)

For the experimental conditions of higher temperature, the nitrogen and carbon percentage in the solid product increased, whilst the content of oxygen and hydrogen diminished. The results are in correspondence with those reported to biochar obtained at different temperatures for pine, poplar and willow sawdust (Calvelo Pereira, Kaal et al.). This behaviour in the variations of oxygen and hydrogen contents can be explained by the fact that at this temperature, one part reacts to form water, which can be up to 70% of the composition of the gases released (Tumuluru, Sokhansanj et al. 2010).

The change in elemental analysis values from biomass to coal can be displayed using a diagram developed by Van Krevelen (1993). Fig. 6 shows the change in the atomic ratios H/C and O/C from *D. cinerea* to torrefied biomass, peat, lignite, and coal. As can be observed in this figure, the *D. cinerea* contains higher H:C and O:C ratios compared to other materials.

There is a tendency of the torrefied material to become similar to coal with regard to its elemental composition, in proportion to temperature increase. So, for the experiments carried out at 290°C, the elemental composition of treated biomass possesses characteristics that are halfway between lignite and peat, with an advantage over the latter whose humidity values are lower. This therefore provides certain energetic benefits.
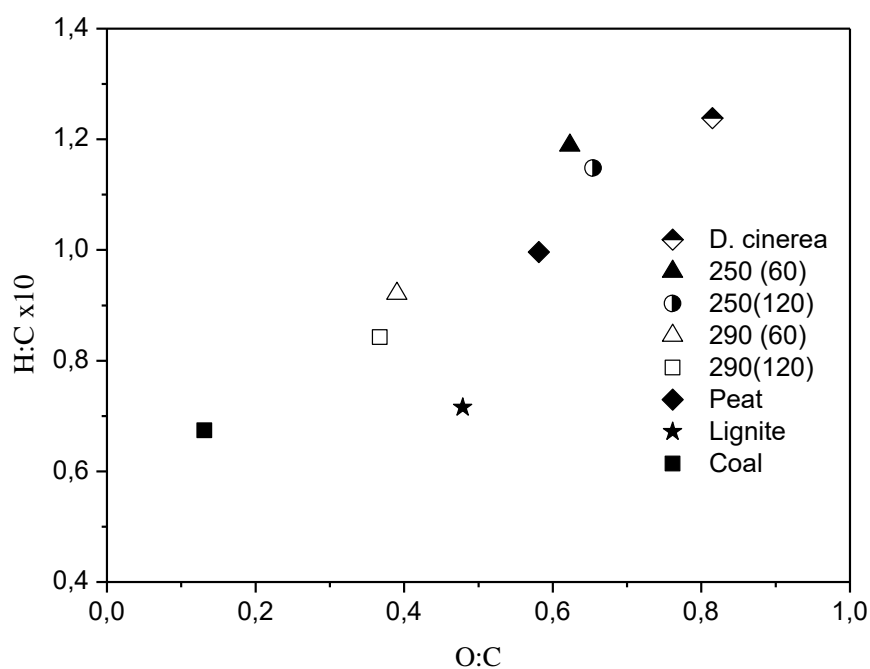
Fig. 5. Van Krevelen diagram for the *D. cinerea* and torrefied biomass, peat (Cummins, McDonnell et al. 2006), lignite (Pipatmanomai, Fungtammasan et al. 2009) and coal (Schaffel, Mancini et al. 2009) at different conditions.

Meanwhile, in fig. 3 it is observed that the biomass loses more oxygen and hydrogen than carbon. The main consequence of this phenomenon is the rise of the calorific capacity from 7.8 to 27.3% of their values regarding the untreated biomass. The HHV's for 290(60) and 290(120) are higher than that of peat (22.94 MJ kg^{-1}), similar to that of lignite (24.63 MJ kg^{-1}) but lower than that of coal (33.8 MJ kg^{-1}). HHV's for the coal, lignite and peat were estimated by the Channiwala method (1992). The elemental analysis was reported by Cummins et al. (2006), Pipatmanomai et al. (2009) and Schaffe et al. (2009), respectively.

Simultaneously, in the torrefaction process, the biomass is dried, so the humidity content of the torrefied product is generally too small (around 3.5%) and also has hydrophobic properties. The main explanation for this new trait is that during the

dehydration reactions, the OH groups of the biomass are destroyed, and the torrefied product loses its capacity for forming hydrogen bridges with water. Similarly, other unsaturated structures are formed in the process, which are non-polar and hydrophobic to a certain extent. At the same time, given this new characteristic, a new more stable material is formed, which can be preserved for longer periods with few variations in its traits (Sadaka and Negi 2009).

3.3. Thermogravimetric characterisation of torrefied biomass

The torrefied materials were submitted to a thermogravimetric study in an inert atmosphere and their main devolatilisation characteristics were determined with the objective of understanding the decomposition process of the new materials obtained regarding the original biomass. The main mass loss process occurred in the range of 220 to 550 $^{\circ}$C, with peaks of maximum devolatilisation rate between approximately 270 and 350 $^{\circ}$C. This is mainly attributed to the decomposition of hemicellulose, cellulose and lignin (Yang, Yan et al. 2007). Table 4 shows the results of the main thermogravimetric characteristics according to Gronli, Várhegyi et al. (2002) for the *D. cinerea* and torrefied material at 250 and 290 $^{\circ}$C.

Table 4. Main characteristics of the devolatilisation of untreated and treated *D. cinerea* at a heating rate of 10 $^{\circ}$C min^{-1}

Material	T_{onset} ($^{\circ}$C)	T_{peak} ($^{\circ}$C)	$(dw/dT)_{peak}$ ($^{\circ}$C^{-1})	w_{peak} (%)	$w_{700^{\circ}C}$ (%)
D.cinerea	229	332	-0.0080	62.3	26.2
250(60)	265	346	-0.0080	68.8	27.2
290(60)	290	336	-0.0048	85.8	41.1

As expected, the initial temperature of degradation (T_{onset}) is higher for torrefied materials and its value is close to the temperature of those previously treated, because at lower temperatures a part of the original biomass has been devolatilised. The

temperature value where the maximum conversion values are obtained (T_{peak}) does not vary significantly for the three materials. For the treated biomass at 250 °C the variation of the value of (dw/dT) $_{peak}$ is lower than that of the material that has been exposed to more severe temperature conditions, as compared to *D. cinerea*. The conversion percentages obtained are inversely proportional to the torrefaction temperature, which is explained by the fact that a part of the volatile material was already degraded in such a process.
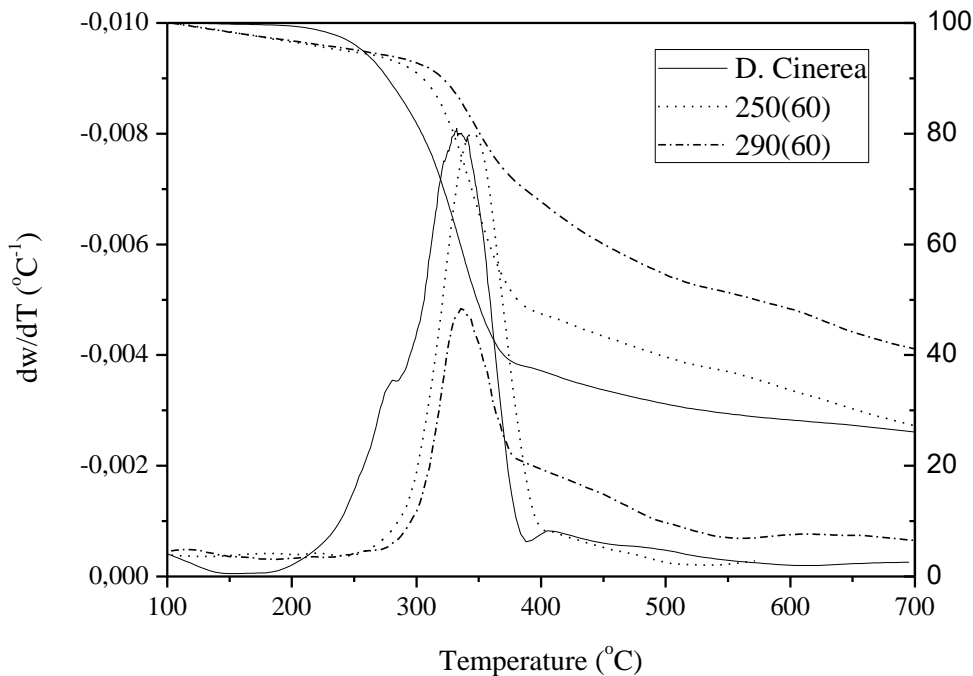

Fig. 6. DTG-TG curves of untreated and treated *D. cinerea* obtained at 250 y 290 °C by 60 min, at heating rate 10 °C min^{-1} inert atmosphere.

As previously mentioned, the degradation process of the lignocellulosic materials is characterised by presenting three zones or peaks of decomposition, which are generally identified with their main pseudo-components hemicellulose, cellulose and lignin in that order (Caballero, Conesa et al. 1997, Orfão, Antunes et al. 1999, Gronli, Várhegyi et al. 2002, Yang, Yan et al. 2007). The peaks attributed to the pseudo-components can be

observed in Fig. 6 for the DTG curve corresponding to *D. cinerea*. However, the devolatilisation curves of the torrefied materials are shown in the same figure, whose characteristic is the absence of the first decomposition peak present in the degradation of the untreated biomass. This suggests that at the temperatures at which the materials have been exposed, a great part of the hemicellulose present in *D. cinerea* has reacted (Yang, Yan et al. 2007). Furthermore, a slight increase in the range of the second conversion zone is noticed for the material obtained at 250 $^{\circ}$C, presumably because the torrefaction temperature has only modified the structure of cellulose and lignin to a lower extent. On the other hand, for the torrefied biomass at 290 $^{\circ}$C, the change of the second and third degradation zones is noticeable, mainly for the peak associated to lignin, where a higher reactivity of can be appreciated. The increase in the third peak can be attributed to a higher decomposition reactivity of the lignin as a consequence of modifications to its molecular structure and the thermo-decomposition of the carbon material formed from the thermo-decomposition mainly of hemicellulose in the torrefaction process at 290 $^{\circ}$C.

4. Conclusions

According to the results obtained in design of experiment 2^2, it was concluded that the temperature, reaction time and their interaction were significant but the highest effect was associated to temperature on solid percentage in the torrefaction process. Meanwhile, the temperature factor only had a significant effect when the increment of HHV as a dependent variable was considered. A good linear relationship between the analyse variables was found. In the results of the elemental analysis performance on the torrefied product, it was appreciated that the most diminished element was oxygen. This brings about an increase in energy density. Thermogravimetric characterisation and

DTG – TG curves of the torrefied material suggest that the pre-treated material has been modified chemically and structurally.

Acknowledgements

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