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ORIGINAL

Experiments on torrefaction of *Dichrostachys cinerea* wood: two-level factorial design and thermogravimetric analysis

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Abstract The aim of this study was to determine the effect of the temperature and reaction time variables on the solid yield and the increment of heating values and composition of torrefied *Dichrostachys cinerea* wood by using a factorial experiment design and thermogravimetric analysis. The significant factors were identified by means of a two-level factorial design 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 HHVs of 14.92 and 30.31% under the conditions of 120 min at 250 and 290 °C, respectively. Thermogravimetric characterisation and DTG–TG curves of the torrefied material suggest that the pretreated material has been modified chemically and structurally.

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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 position of biomass, as the only renewable source that is a 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 et al. 2011). Woody biomass is preferred over food crops because of many reasons: from energy-related ones 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 (Domec et al. 2017; Van der Stelt 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*) (Abreu et al. 2010; Bridgeman et al. 2008; de Sales et al. 2017; Fernández et al. 2015; Monedero et al. 2017; Pérez et al. 2011).

This study focuses on the latter species *(Dichrostachys cinerea).* 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 et al. 2008; Pedroso and Kaltschmitt 2012). From the viewpoint of energy, this means a theoretical potential of 700 × 10 GJ. The elemental and proximate analysis, as well as the main characteristics of *D. cinerea* devolatilisation, was previously determined and discussed by Abreu et al. (2010). The authors demonstrated that this biomass possesses the appropriate characteristics to be used as an energy source, given that it has a caloric value that is higher than or equal to 19,100 kJ kg^{-1}, 3.4% ashes and a melting temperature of 1460 °C, as well as low contents of chlorine and sulphur. Moreover, they determined the main devolatilisation parameters (percentage of weight loss, temperatures and degradations rates) and compared them to other lignocellulosic materials, such as corn stover and sugarcane bagasse. Similar results were obtained by Pedroso and Kaltschmitt (2012). Their study concluded that *D. cinerea* wood can be used as a promising solid biofuel. Furthermore, the authors compared the *D. cinerea* properties with other types of biomass: sugarcane bagasse, German beech, poplar, wheat straw and rice straw. They found that the combustion of *D. cinerea* releases fewer emissions. A simultaneous modelling of pyrolysis and combustion processes of *D. cinerea* and the determination of the kinetic parameters by means of thermogravimetric analysis were investigated by Abreu 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 came to the conclusion that *D. cinerea* represents the biomass source with the highest potential, followed by sugar cane bagasse. Three scenarios were considered to extend electricity generation from biomass in sugar factories beyond the sugarcane milling season (Ulrich 1984). However, the use of torrefied material from *D. Cinerea* was not assessed as a solid fuel.

Further, 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 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 considerable. Wood and other biomass can be treated in different ways to provide better properties like fuel material (Prins et al. 2006). A recent study was carried out by Wilk and Magdziarz (2017), who analysed the effect of different pretreatment processes of hydrothermal carbonisation, torrefaction and slow pyrolysis on the properties of *Miscanthus giganteus*. The authors obtained rises of carbon content of 36, 34 and 80% for the hydrothermal carbonisation, torrefaction and slow pyrolysis, respectively. 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 (Bach et al. 2017; Wang et al. 2017a, b). In a recent research conducted by Li et al. (2017) on the structural and thermal properties of *Populus tomentosa* during carbon dioxide torrefaction, the authors demonstrated that the torrefaction led to substantial changes in structural properties, increasing thermal stability and the combustion reactivity from 4.13%/(min °C) in the raw material to 4.98%/(min °C) for the sample subjected to torrefaction at 280 °C for 75 min. Torrefaction is a thermal decomposition process characterised by its low heating rate, inert atmosphere and a range of temperatures between 200 and 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 et al. 2011). Various studies on the torrefaction of different types of biomass have been published such as: wheat straw (Mei et al. 2016); olive stones (Sánchez and San Miguel 2016); and forest residues (spruce and birch) (Bach et al. 2016). Nevertheless, a study about *D. cinerea* torrefaction as a biofuel was not found in the studied literature.

On the other hand, a two-level factorial design allows for determining the relative influence of several factors in this process within the studied range, whilst requiring fewer experimental runs than traditional experimental methodology. Systematic errors can also be eliminated by using a design of experiment (DOE) approach

(Fegade et al. 2013). An advantage of the DOE methodology is its ability to recognise significant interactions between factors and their influence on the response variables. Generally, these conclusions are not found by means of traditional methods of experimentation.

The aim of this study was to contribute to the knowledge of biomass in order to obtain a better application of the biomass obtained from *D. cinerea* as a fuel. The effect of the temperature and reaction time variables on the solid yield and the increment of heating values and composition of torrefied *Dichrostachys cinerea* wood were also determined by using a factorial experiment design and thermogravimetric analysis.

Materials and methods

Chemical–physical characterisation

The raw biomass samples used in this study originated from the central region of Cuba and were transported to the Biomass Laboratory of Agricultural, Food and Environmental Sciences Department of the Polytechnic University of Marche (UNIVPM), where the experimental analysis was carried out. For the preparation of the *D. cinerea* samples, the norms of the European Committee for Standardisation (CEN/TS 14780) were used. They consist of stabilising the samples in a stove for 48 h at a temperature of 45 °C and subsequently, the samples were reduced to particle sizes of approximately 1 mm by using a cutting mill model (Retsch M2000). The moisture content of the samples was determined in a stove at 105 °C for 24 h (CEN/TS 14774). Volatile matter and ash were determined in a TGA Leco 701 instrument according to the standards of CENTS 15148 and CEN/TS 14775, respectively. The first consists of maintaining the samples (approximately 1 g) at 900 °C for 7 min and the ash at 550 °C for 4 h. The fixed carbon was determined as difference.

The chemical–physical characterisation of *D. cinerea* has previously been analysed (Abreu et al. 2010). The elemental analysis of torrefied wood was determined in accordance with the standard CEN/TS 15104. For determination of elemental analysis, an equipment model PerkinElmer 2400 CHNO/S was used. The determination of the high heating value (HHV) was carried out in a calorimetric bomb (IKA WERKER KV 500) and under the conditions of the standard CEN/TS 14918.

Torrefaction experiments in a pilot plant reactor

Torrefaction experimental procedure

It is possible to investigate a number of variables and their effects using a factorial or screening design. The simplest factorial design involves two factors, each at two levels (2^2). The advantage of the two-factor study is the reduction in the quantity of experimental runs, whilst obtaining the same precision for effect estimation in comparison with other designs. The point is that a factorial design provides contrasts of averages, thus providing statistical power to the effect estimates. It reveals “interactions” of factors, which often proves to be the key to understanding a process (Anderson and Whitcomb 2016). The experimental planning for this study was performed by means of a two-level factorial design (TLFD) type (2^2) with two replicates. In this way, the influence of the two factors on the solid yield and increment of HHV was considered. Daniel’s half-normal plot method of effects was used for determining the significant effects, in accordance with Whitcomb and Oehlert (2007), which allowed for the identification and quantification of the significant factors on response variables. The statistical software Design Expert version 10.0.2 (Stat Ease, USA) was used, as well as ANOVA for the analysis of the results. Design Expert randomises 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:

$$\text{increment in HHV} = \frac{\text{HHV}_{\text{tor}} - \text{HHV}_{\text{raw}}}{\text{HHV}_{\text{raw}}} \times 100 \quad (1)$$

HHV_{tor} 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 in Table 1.

Description of equipment

The torrefaction experiments were performed in the laboratory of the Department of Chemical Engineering at the University of Alicante, Spain. This reactor was used in previous thermodecomposition research (Conesa et al. 2004). A scheme of the reactor system is represented in Fig. 1. The system is made up of five main zones.

Approximately 40 g of biomass is 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.

Table 1 Level of variables chosen for the TLFD

Independent variable	Uncoded and coded variable level		
	Symbol	Low − 1	High 1
Torrefaction temperature (°C)	A	250	290
Residence time (min)	B	60	120

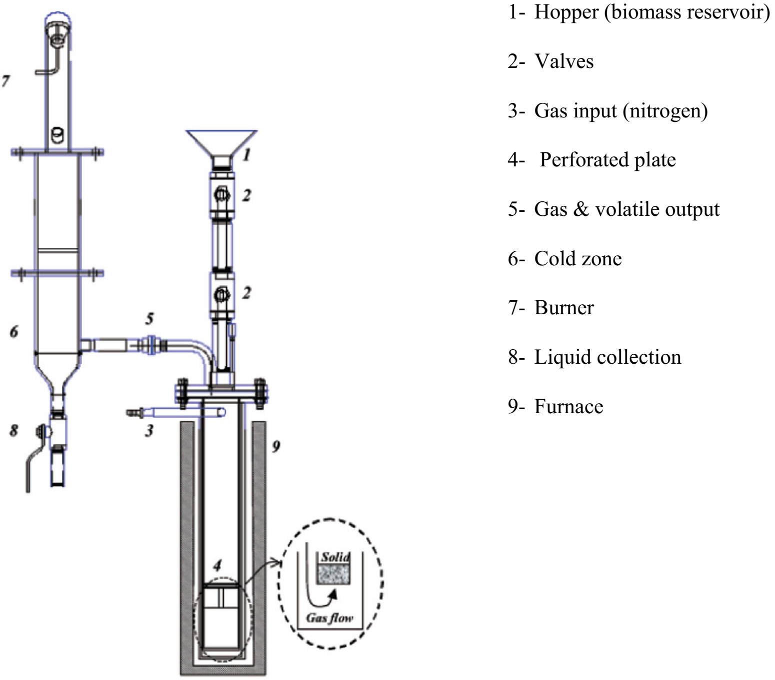

Fig. 1 Schematic of the reactor system

The temperature was 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.

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 heating programme in order to establish an inert environment.

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

> "T_{onset} temperature was calculated from the extrapolation of the partial peak of the decomposition of the hemicellulose, which marks the beginning of the active zone of thermodecomposition."

$(\mathrm{d}w/\mathrm{d}T)_{\text{peak}}$ and T_{peak} are the maximum overall decomposition rates, mainly associated with the cellulose decomposition and their corresponding temperature, respectively.

T_{offset} is the extrapolated temperature of the ($\mathrm{d}w/\mathrm{d}T$) curve. This value marks the end of the cellulose decomposition.

w_{peak} and $w_{700\ ^\circ\mathrm{C}}$ are weight fractions expressed in percentages at the temperatures of T_{peak} and 700 °C, respectively.

Results and discussion

Torrefaction experiments in pilot plant reactor

Factors affecting solid yield and increment in HHV

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 in this plot. Starting on the right, the largest effects are seen. Temperature, residence time and their interaction have a significant effect on solid yield (Fig. 2a), 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. 2b).

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

$$\text{Solid yield} = 69.07 - 14.89A - 3.75B + 1.99AB \quad (2)$$

$$\text{Increment in HHV} = 19.25 + 8.26A + 1.12B - 0.24AB \quad (3)$$

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

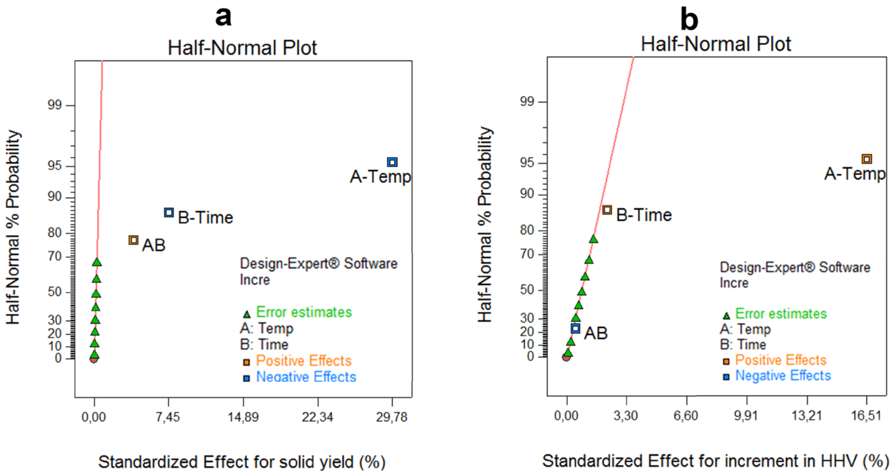

Fig. 2 Half normal versus effect plots for solid yield (**a**) and increment in HHV (**b**)

Table 2 ANOVA adjustment coefficient for yield and increment in HHV

	Solid yield	Increment in HHV
R^2	0.9994	0.959
Adj R-Squared	0.9991	0.9437
Pred R-Squared	0.9986	0.9078
Adeq Precision	135.91	15.39

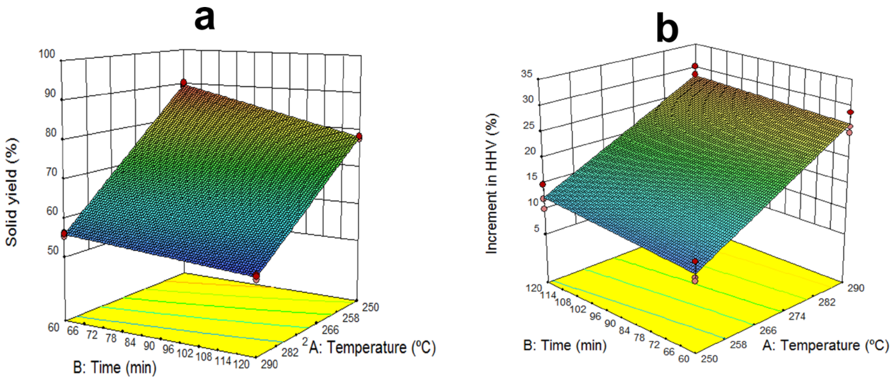

Fig. 3 3D surface plots of residence time and temperature interaction for the response variables solid yield (**a**) and increment in HHV (**b**)

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, being less than 0.2, as suggested by Anderson and Whitcomb (2015).

The coded model (Eqs. 2, 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.

As can be seen in both response variables (solid yield and increment in HHV), temperature had an effect higher than residence time. The variations in solid yield were more sensitive to changes in temperature than when residence time was varied. At longer residence times, the values of the independent variables remained almost constant for the same temperature. These results are in accordance with those obtained by Li et al. (2017) in the carbon dioxide torrefaction of *Populus tomentosa*. As expected, 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 et al. 2015). On the other hand, for torrefied biomass, an increment in HHV of 14.92 and 30.31% was achieved under the conditions of 120 min and 250 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 versus solid yield was created as shown in Fig. 4. These two variables show a good linear relationship with R-Squared equal to 0.92.

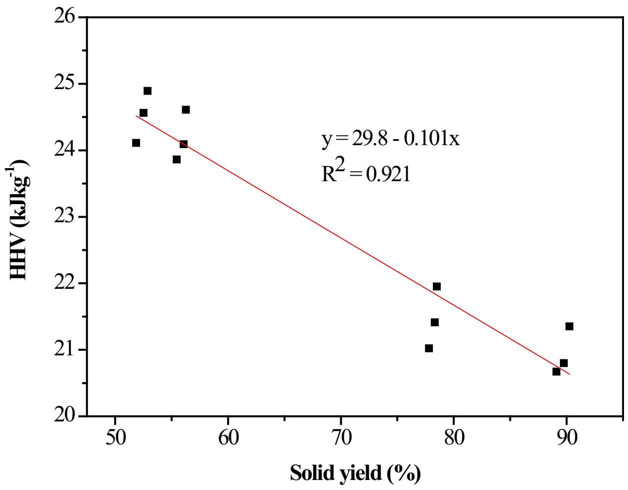

Fig. 4 HHV versus solid yield

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

	D. cinerea[*]	250 (60)	250 (120)	290 (60)	290 (120)
Ultimate analysis, wt% (daf)					
C	51.16	56.41	55.57	66.09	67.51
H	6.34	6.71	6.38	6.09	5.69
N	0.82	1.74	1.70	2.04	2.02
O[**]	41.69	35.14	36.36	25.78	24.79
Proximate analysis, wt% (daf)					
Fixed carbon	14.78	23.90	24.43	36.15	38.34
Volatile matter	77.26	65.06	67.04	52.50	51.26
Ash	3.4	6.81	7.06	7.78	7.81
Moisture	4.56	3.63	3.45	3.53	2.94

daf dry ash free basis

* (Abreu et al. 2010), ** oxygen calculated by difference

Chemical–physical characterisation of torrefied biomass

To characterise the torrefied material obtained and to be able to compare the values with the untreated material, the ultimate and proximate analysis of the samples was determined. Table 3 shows the values.

For the experimental conditions of higher temperature, the nitrogen and carbon content (wt%) in the solid product increased, whilst that of oxygen and hydrogen diminished. The results are in line with those reported for biochar obtained at different temperatures for pine, poplar and willow sawdust (Calvelo Pereira et al. 2011). 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 et al. 2010). The fixed carbon and volatile matter for the raw and torrefied materials were determined (see Table 3). These parameters are two important properties, usually used to evaluate the quality of solid fuels (Wilk and Magdziarz 2017). *D. cinerea* without thermal pretreatment presents a low volatile matter content (77.26%), in comparison with other woody species: willow (87.6%), *Quercus rotundifolia* (83.6%), *Pinus halepensis* (82.5%) and *Eucalyptus saligna* (82.0%) (Bridgeman et al. 2008; Cordero et al. 2001). However, this parameter is associated with a diminution of energy efficiency and harmful emissions when it is used directly (Magdziarz et al. 2011; Wilk and Magdziarz 2017). The torrefaction process at 290 °C may reduce the volatile matter content by up to 32.1% and 33.7%, at 60 and 120 min, respectively. This confirms the design of experiment results regarding the lesser influence of residence time with respect to the temperature variable on the characteristics of torrefied material. As can be seen in Table 3, the fixed carbon value increased when temperature and residence time increased, from 14.78% as raw material to 38.34% as torrefied material at 290 °C and 120 min. A similar trend was observed for the ash content.

The change in elemental analysis values from biomass to coal can be displayed using a diagram developed by Van Krevelen (1993). Figure 5 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, *D. cinerea* contains higher H/C and O/C ratios compared to other materials.

The torrefied material has a tendency 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

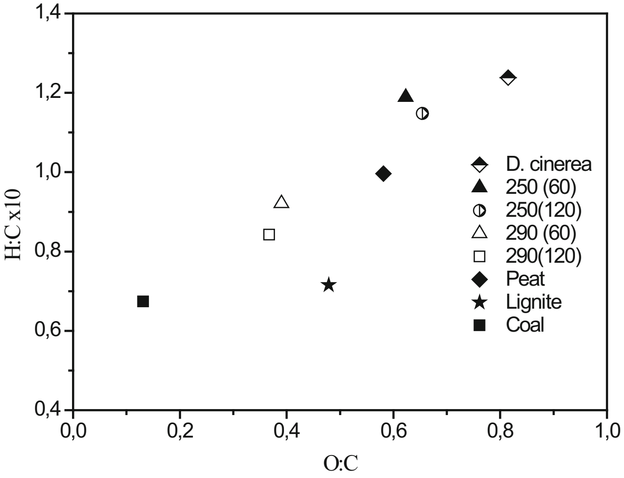

Fig. 5 Van Krevelen diagram for the *D. cinerea* and torrefied biomass, peat (Cummins et al. 2006), lignite (Pipatmanomai et al. 2009) and coal (Schaffel and Mancini 2009) at different conditions

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.

Meanwhile, in Fig. 5 it can be 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 HHVs for 290(60) and 290(120) are higher than that of peat (22.94MJkg^{-1}), similar to that of lignite (24.63MJkg^{-1}) but lower than that of coal (33.8MJkg^{-1}). HHVs for coal, lignite and peat were estimated by the Channiwala method (Channiwala and Parikh 2002). The elemental analysis was reported by Cummins et al. (2006), Pipatmanomai et al. (2009) and Schaffel and Mancini (2009), respectively.

In the torrefaction process, the biomass is dried, so the humidity content of the torrefied product is generally too low (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 to form hydrogen bonds 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).

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 °C, with peaks of maximum devolatilisation rates between approximately 270 and 350 °C. This is mainly attributed to the decomposition of hemicellulose, cellulose and lignin (Yang et al. 2007). Table 4 shows the results of the main thermogravimetric characteristics according to Gronli et al. (2002) for *D. cinerea* and torrefied material at 250 and 290 °C.

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

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

Material	T_{onset} (°C)	T_{peak} (°C)	$(dw/dT)_{\text{peak}}$ (°C^{-1})	W_{peak} (%)	$W_{700\ °C}$ (%)
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

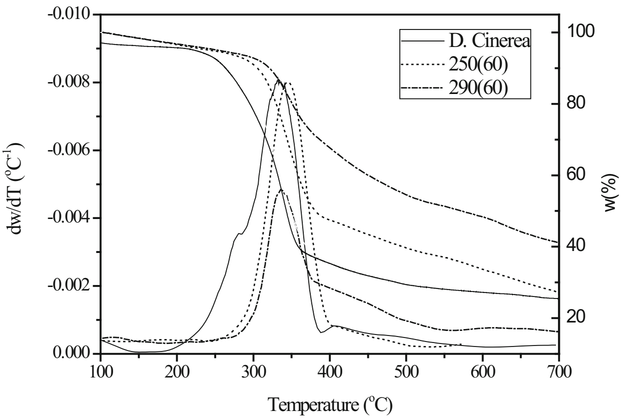

Fig. 6 DTG–TG curves of untreated and treated *D. cinerea* obtained at 250 and 290 °C for 60 min, at heating rate 10 °C min^{-1} inert atmosphere

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 $(\mathrm{d}w/\mathrm{d}T)_{\text{peak}}$ 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 has already been degraded in such a process.

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 et al. 1997; Gronli et al. 2002; Orfão et al. 1999; Yang et al. 2007). The peaks attributed to the pseudo-components can be observed in Fig. 6 for the DTG curve corresponding to *D. cinerea*. 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 to which the materials have been exposed, most of the hemicellulose present in *D. cinerea* has reacted (Yang et al. 2007). Furthermore, a slight increase in the range of the second conversion zone is noticed for the material obtained at 250 °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 °C, the change in the second and third degradation zones is noticeable, mainly for the peak associated with lignin, where a higher reactivity can be appreciated. The increase in the intensity of the third peak can be explained by the relative accumulation of lignin, also as a consequence of modifications of its molecular structure and the thermodecomposition of the carbon material formed from the thermodecomposition, mainly of hemicelluloses, in the torrefaction process at 290 °C.

Conclusion

By means of TLFD type 2^2 methodology, the relative impact of the selected factors on solid yield and increment of HHV was quantified. For both, the coefficient for temperature was higher. According to the design of experiment results, it was concluded that the temperature, reaction time and their interaction were all significant, but the highest effect was associated with 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 analysed variables was found. The results of the elemental analysis performed on the torrefied product showed 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.

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