INFLUENCE OF TORREFACTION ON SOME CHEMICAL AND ENERGY PROPERTIES OF MARITIME PINE AND PEDUNCULATE OAK

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This study investigated the influence of heat treatment on the chemical composition and energy properties of maritime pine (*Pinus pinaster*) and pedunculate oak (*Quercus robur*). Samples were treated in a new experimental device at 220, 250, or 280 °C for 1 or 5 hours. Chemical and energy analyses were performed using standard methods. Our results clearly demonstrated an increased degradation of the material due to the combined effects of temperature and treatment duration. This mass loss was basically due to degradation of acid-soluble materials. The energy analysis showed that the fixed carbon content and higher heating value increased, for both species, whereas the volatile matter content decreased with increased extent of treatment (cumulated effects of temperature and time). In the range of temperature and duration studied here, the dimensionless energy properties for both species obeyed the same functions of overall mass loss. The relationships obtained allow quantification of the increase in wood energy concentration due to torrefaction. Mass loss is an excellent indicator of treatment extent. Analytical expressions allowing the prediction of energy and chemical properties as a function of overall mass loss, within the range of treatment extents studied here, are provided.

Keywords: Biomass; Chemical analysis; Energy yield; Heating value; Proximate analysis; Torrefaction

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INTRODUCTION

In answer to the fossil fuel crisis and global warming, the use of renewable energy is being promoted worldwide. The conflict between bioenergy and food production has encouraged the use of lignocellulosic biomass for biofuel production, which has given rise to numerous R&D projects devoted to the so-called 2nd generation biofuels. This paper focuses on wood, although various other plant sources such as straw, agricultural residues, and other wastes can be used. However, it has to be kept in mind that, somewhere between the field and the biorefinery, several preconditioning steps are usually necessary. Similar steps are required when the biomass is used as energy source or as renewable carbon (e.g. charcoal in the steel industry). One such process, torrefaction, has been recommended as an interesting way to enhance biomass properties by water removal, reduction of the hygroscopic range, and increased grindability.

Torrefaction consists of subjecting wood to temperature levels between 200 and 280 °C in the absence of oxygen (Bourgeois 1989). During this process, the cell walls are degraded, and the nature of the resulting product lies between that of wood and charcoal. On the whole, the effects of torrefaction depend on the heating process, with temperature level and duration as key parameters. This degradation of the cell walls implies changes in technological properties. Numerous studies have already investigated the modification of different properties such as colour (Bekta and Niemz 2003), fungal durability (Hakkou et al. 2006), reduction of hygroscopicity, and the subsequent shrinkage decrease (Almeida et al. 2009). Torrefaction also affects the mechanical properties (Unsal and Ayrilmis 2005; Esteves et al. 2007), facilitating wood grinding, and thus the required energy cost of this operation (Bergman et al. 2005; Govin et al. 2009).

Fewer studies have systematically investigated the energy properties of heat-treated wood, which are of utmost importance if the resulting product is to be used for energy production. The mass yield is also very important for optimizing the overall chain between the field and the desired product or service.

This study is therefore devoted to the modification of energy characteristic of a softwood species, maritime pine (*Pinus pinaster*), and a hardwood species, pedunculate oak (*Quercus robur*), subjected to different treatment extents. In addition, a set of chemical analyses was performed to quantify the alteration of acid-soluble and acid-insoluble materials in the two species, in order to better understand these modifications and eventually permit a predictive approach in other species.

MATERIAL AND METHODS

Material Selection and Preparation

The maritime pine (*Pinus pinaster*) was about 20 years old and came from south-east France. The pedunculate oak (*Quercus robur*) was about 35 years old and came from eastern France (Brin Forest, Nancy). Seven defect-free samples per species, measuring 5 × 1.5 × 20 cm3 (R,T,L), were cut from the sapwood part of the boards. The annual ring width for each sample was about 3 mm. The samples were stored under laboratory conditions before being oven-dried at 103 (± 2 °C) until equilibrium. The anhydrous masses were then determined to the nearest 0.001 g using a digital balance. Samples were stored in a desiccator containing silica gel until torrefaction.

After heat treatment (see “torrefaction procedure” paragraph), a portion of each sample was crushed into powder. The powder was then sifted through a 40 mesh sieve and a 6 mesh sieve. The final particle size was less than 0.21 mm.

The test material had an average basic wood density (oven-dry mass to green volume) of 563 kg/m^3 for maritime pine (coefficient of variation (CV) of 3%) and of 603 kg/m^3 for penduculate oak (CV of 4%).

Torrefaction Procedure

In order to assess the properties modifications due to the heat treatment, the treatment itself is of utmost importance and has to be accurately applied. In the present study we used a device specifically developed in our laboratory for this purpose (Colin et al. 2007). The whole atmosphere of a hermetically closed *Memmert UFP400* chamber is controlled by a nitrogen flow rate to reduce the oxygen level. Consequently, the samples benefit from the high heat exchange coefficient ensured by the powerful fan situated inside the chamber (c.a. 35 W.m^{-2}.K^{-1}). Such a good heat transfer reduces the difference between the gas and the sample temperature. For each test, the oxygen level remained below 1%. As this level is measured on the gas flow leaving the chamber by an Arelco ZOA 100 sensor, one can guarantee such a low level throughout the chamber. The gas temperature is measured nearby the samples using a calibrated thermocouple.

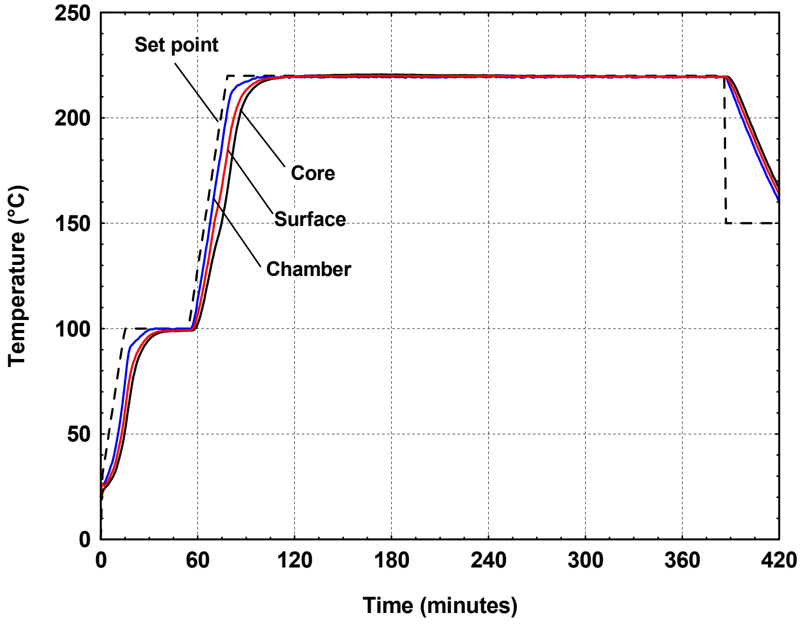
Thanks to an *Agilent* data acquisition system piloted by a *Visual Basic* program, the heating rate was controlled, and the temperature, oxygen level, and sample mass were continuously recorded. Nitrogen flow rate was controlled thanks to a *Fischer Scientific Bioblock* flowmeter, and during experiments the nitrogen flow rate was about 5L/min. Several heat treatments were conducted at 220, 250, or 280 °C for 1 or 5 hours under nitrogen according to the following protocol: (a) heating rate of 5 °C/min up to 100 °C; (b) plateau at 100 °C for 30 minutes; (c) heating rate of 5 °C/min until the final treatment temperature is reached then maintained at this level for 1 or 5 hours; and (d) decrease in temperature by 2 °C/min down to 150 °C, achieved by opening all the oven valves allowing for a better cooling thanks to a higher nitrogen flow rate.

Figure 1 depicts two contrasted examples of the temperature variations during the test. For each test, the set temperature is the desired temperature as defined by the protocol and the chamber temperature is the actual temperature, as recorded by the thermocouple. Thanks to an adapted regulation algorithm put in the Visual Basic program, the difference between these temperatures remains very small. The surface and core temperatures are simulated by a comprehensive computational model (Turner et al. 2010). In this simulation, the actual chamber temperature was used as boundary conditions.

At 220 °C no significant exothermic reactions took place. Consequently, the sole differences between the chamber temperature and the sample temperatures resulted from the two heat transfer resistances: convective transfer within the boundary layer and conductive heat transfer within the sample. As can be seen on Fig. 1, these differences existed only during the transient periods (positive value before a plateau and negative value at the end of a plateau) and, thanks to the high heat exchange coefficient and the small sample thickness, remained moderate. Therefore, for this favorable test, all temperatures remained very close to the desired level during almost the entire treatment temperature.

At 280 °C the temperature level was high enough to trigger exothermic reactions (Rousset et al. 2006). This explains the thermal overshoot depicted for the sample temperatures, especially the core temperature, at the beginning of the plateau at 280 °C. In our simulation, this overshoot reached almost 12 °C at the core of the sample, but for a very short time. In addition, this value is certainly overestimated, as the kinetics of hemicelluloses embedded in our model is rather too fast (Turner et al. 2010). As a conclusion, even for this worst test (high temperature level and short treatment duration), the temperature levels throughout the sample remained in good agreement with the protocol temperature.

As an assessment of the treatment quality actually obtained in our experimental device, Table 1 summarizes some global data for each test: treatment duration for three temperatures (measured chamber temperature, computed surface and core temperatures), and the temperature overshoot (computed surface and core temperatures). The duration is counted with a tolerance of 3 °C (from $T_{plateau}$ – 3 °C before the plateau to $T_{plateau}$ – 3 °C after the plateau). This table allows us to know exactly the conditions undergone by the sample and to notice that these conditions remained in quite close agreement with the desired conditions.



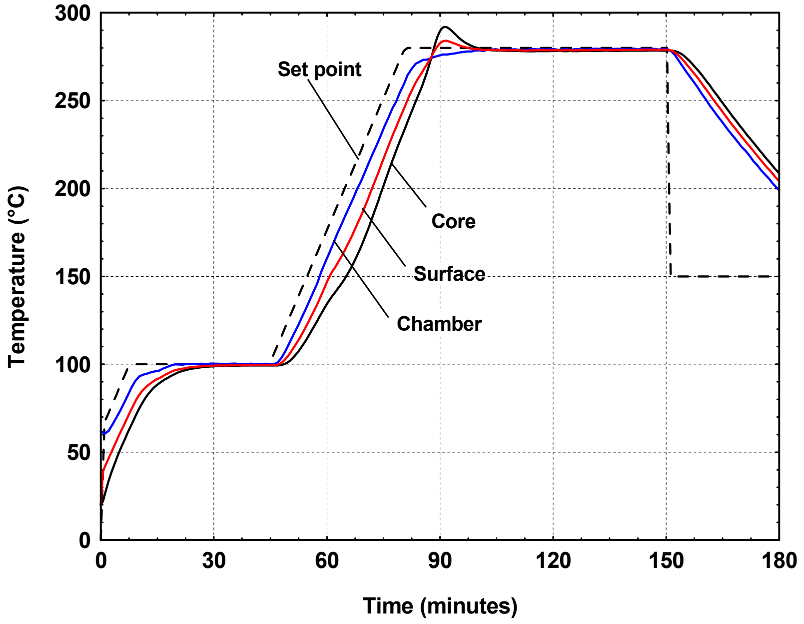


Fig. 1. The temperature evolutions for two contrasted tests (top: 220 °C – 5h and bottom: 280 °C - 1h)

Table 1. Treatment Durations and Maximum Temperatures for the Six Tests Reported in the Present Work

Test	Treatment duration (T_0 – 3°C, minutes)			T_{max} (°C)	
	Chamber	Surface	Core	Surface	Core
220°C – 1 hour	60	54	53	220.2	200.6
220°C – 5 hours	298	293	292	220.1	220.5
250°C – 1 hour	59	58	57	253.7	257.7
250°C – 5 hours	299	296	296	253.7	257.9
280°C – 1 hour	58	64	65	284.0	291.7
280°C – 5 hours	298	304	306	283.9	291.7

For each treatment, the mass loss of torrefied wood was calculated using the following expression,

$$ML = [(M_1 - M_2) / M_1] \text{ x } 100 \qquad (1)$$

where ML is the mass loss (%), M_1 is the initial oven-dried mass of the wood sample before heat treatment, and M_2 is the oven dried mass of the wood sample after heat treatment.

Chemical Properties

Acid-insoluble materials (AIM) and the extractives contents were determined on untreated and heat treated samples. AIM, consisting by a majority of lignin, were measured after wood hydrolysis with sulphuric acid according to the T-22 OM-88 method (TAPPI 1994a). The extractives content (ET) was determined as the content of products soluble in dichloromethane, ethyl-alcohol, and hot water according to the T-204 OM-88 method (TAPPI 1994b). The acid-soluble materials (ASM), consisting by a majority of cellulose and hemicelluloses, was calculated according to,

$$ASM = 100 - ET - AIM \qquad (2)$$

More details concerning the chemical analyses can be found in Brito et al. (2008).

Energy Properties

The fixed carbon and volatile matter contents and the higher heating value (*HHV*) were determined on untreated and torrefied samples. The fixed carbon content and the volatile matter content were measured according to ABNT-NBR-8112 (Determination of ash, volatile matter and fixed carbon in vegetal charcoal) (ABNT, 1986).The higher heating values of untreated and torrefied samples were measured according to the ASTM D5865 standard (ASTM, 2007) (dynamic mode at 25°C) using an adiabatic bomb calorimeter (IKA C2000).

In order to better perceive the effect of heat treatment, dimensionless quantities were defined for the fixed carbon (FC^*) and higher heating value (HHV^*) by dividing the actual value by the corresponding value obtained for untreated samples:

$$FC^* = (FC_t / FC_u) \qquad (3)$$

$$HHV^* = (HHV_t \;/\; HHV_u) \qquad (4)$$

where FC_u is the fixed carbon content of untreated samples, FC_t is the fixed carbon content of torrefied samples, HHV_u is the higher heating value of untreated samples, and HHV_t is the higher heating value of torrefied samples.

The energy yield (η_E) was also determined according to the following formula,

$$\text{Energy yield } (\eta_E) = \eta_M (HHV_t \;/\; HHV_u)_{\text{daf}} \qquad (5)$$

where η_M is the mass yield, which is the untreated oven-dried mass divided by the heat treated oven-dried mass (Bergman 2005), HHV_u is the higher heating value of untreated samples, HHV_t is the higher heating value of torrefied samples, and daf indicates a dry and ash-free basis.

Statistical Analyses

Statistical analyses were conducted using scientific software from SAS (SAS 2002). Untreated and heat-treated woods were subjected to variance analysis (ANOVA) and Tukey test at the 5% probability level.

RESULTS AND DISCUSSION

Mass Loss

Table 2 shows the mass loss of heat-treated maritime pine and oak woods. As expected, the mass loss increased with time and temperature of treatment in both wood species.

Table 2. Mass Loss of Heat-Treated Maritime Pine and Pedunculate Oak

Temperature (°C)	Time (h)	Mass loss (%)
Maritime pine		
Untreated		-
220	1	5.5
220	5	6.0
250	1	11.0
250	5	16.0
280	1	23.5
280	5	33.3
Pedunculate oak		
Untreated		-
220	1	5.7
220	5	11.4
250	1	19.0
250	5	23.4
280	1	32.9
280	5	48.7

The duration of treatment always had a considerable impact on the mass loss, the sole exception being in the case of maritime pine at 220 °C, for which the additional 4 hours only slightly increased the mass loss (5.5% after 1 hour and 6 % after 5 hours). Due to its ability to consider the cumulated effect of both temperature level and treatment duration into consideration, the mass loss is a good indicator of the extent of treatment (Almeida et al. 2010). A significant difference was apparent between the two species: the mass loss for oak was always higher than for pine for a given treatment level. For example, the more severe treatment (280°C; 5h) caused a mass loss of 33% for maritime pine compared with a mass loss of 49% for oak wood. As shown in the following paragraph, the higher mass loss of oak is due to the easier chemical degradation of hardwood.

Chemical Properties

Results of the chemical analyses are summarized in Table 3. The acid-soluble and acid-insoluble materials of untreated maritime pine and oak were similar to those reported in the literature. For example, Kollman et al. (1965) reported a holocellulose content of 73.2% and a lignin content of 22.2% in oak, and Carvalho (1960) found a holocellulose content of 68.1% and a lignin content of 36.2% in maritime pine.

For both species, our data indicate a dramatic reduction of acid-soluble material content with increasing torrefaction extent. According to the literature, the decrease in acid-soluble material content is essentially due to the reduction of hemicelluloses, which begins to be significant at temperatures above 180 °C (Tjeerdsman 1998; Sivonen 2002). On the contrary, cellulose is thermally more stable. Its degradation starts at about 230 °C but becomes significant only at temperature levels above 300 °C (Repelin 2006). This is consistent with the values obtained for the more severe treatment applied in the present work (280 °C for 5 hours): degradation of the remaining acid-soluble material (28.8 and 11.9% respectively for pine and oak) is only possible with a significant degradation of cellulose, in addition to that of hemicelluloses. Indeed, the cellulose content of untreated wood ranges from 42% in softwood to 45% in hardwood (Thomas 1977).

Table 3 Chemical Analyses of Maritime Pine and Oak Woods

Temperature (°C)	Time (h)	Acid-soluble material (%)		Acid-insoluble material (%)		Extractives (%)	
		M	SD	M	SD	M	SD
Maritime pine							
Untreated		65.31a	0.03	29.3a	0.3	5.4a	0.3
220	1	56.4b	0.2	35.4b	0.1	8.2b	0.3
220	5	60.4c	0.4	34.0c	0.5	5.59a,c	0.04
250	1	56.4d	1.0	37.8d	0.9	5.8c	0.1
250	5	50.6e	0.4	44.0e	0.3	5.4a	0.1
280	1	45.9f	0.4	49.9f	0.2	4.1d	0.6
280	5	28.8g	0.2	65.8g	0.3	5.4a	0.1
Pedunculate oak							
Untreated		74.4a	0.1	17.92a	0.02	7.7a	0.1
220	1	66.7b	1.2	22.6b	1.0	10.7b	0.2
220	5	62.5c	0.8	27.6c	0.3	9.9c	0.5
250	1	55.2d	0.3	35.1d	0.1	9.7c	0.1
250	5	52.8e	1.1	40.5e	0.6	6.7d	0.5
280	1	46.0f	2.0	47.0f	2.0	6.9d	0.1
280	5	11.9g	1.5	82.5g	1.6	5.6e	0.1

S.D. : Standard deviation (%); M: Means of duplicated sample; a : Means followed by the same letter are not significantly different (Tukey, α=5%)

Acid-insoluble material content increased linearly in both species, with an increase of mass loss due thermal treatment (R^2=0.97 for pine wood, R^2=0.94 for oak wood). Of course this was not due to acid-insoluble material production but was a side-effect of the decomposition of hemicelluloses and, to a lesser extent, cellulose content. According to Avat (1993), some products derived from the thermal degradation of carbohydrate could also be present and so increase the acid-insoluble material content. Indeed, the reaction between furfural, from hemicelluloses degradation, and lignin phenolic compounds can give some acid-insoluble product, which increase the acid-insoluble material content. Concerning the cellulose degradation, Agrawal (1988) attested that low temperatures of pyrolysis (below 280 °C) are marked by a scission reaction, which favors crosslinking, as well as aromatization reactions leading to the formation of a solid product (charcoal) having a high content of lignin. In the present work, Agrawal's conclusions would concern the more severe treatments. Within the range of temperatures used in this study, lignin is practically inert to thermal degradation. Only lignin condensation occurs, which would also increase the acid-insoluble material content (Avat 1993).

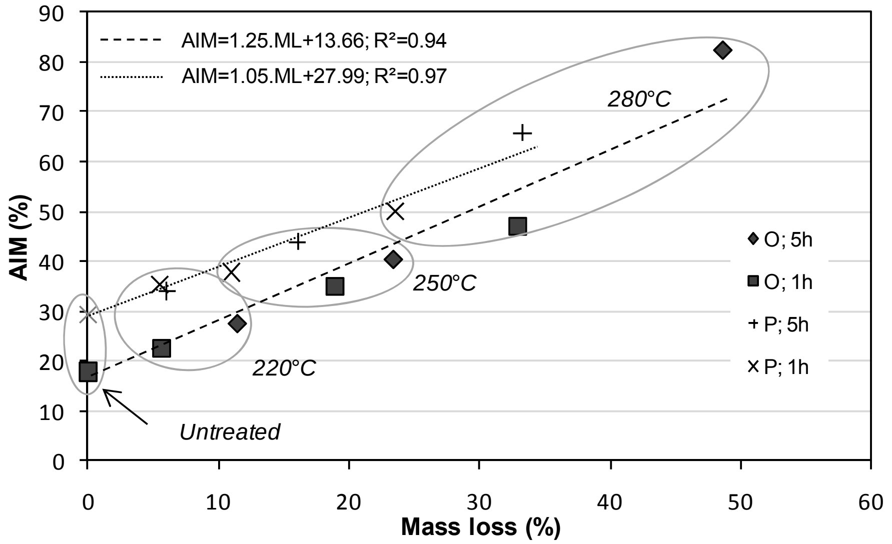


Fig. 2. Acid-insoluble material (AIM) of heat-treated maritime pine (P) and pedunculate oak (O) as a function of mass loss. Data grouped in each circle were subjected to the same temperature of treatment.

Figure 2 shows that the acid-insoluble material content increased more rapidly in oak than in pine. Hardwood hemicelluloses are more sensitive to thermal degradation (Kamdem 2002), giving more degradation products such as furfural. As noted in a previous paragraph, this molecule can react with lignin phenolic compounds, giving some acid-insoluble compounds. It can also be supposed that acetic acid from acetate group is present in hardwood species such as oak. This could partially explain the behaviour of the acid-insoluble material, which was proportionally greater for oak. The observed differences might also be due to differences in the nature of lignin between the two species. Hardwood lignin contains both guaiacyl and syringyl units, whereas softwood only contains guaiacyl units. Avat (1993) showed that condensation of the syringyl units occurred more readily than for the guaiacyl units. Thus, the greater increase of acid-insoluble material in oak than in pine may also be explained by higher condensation of pine’s lignin, which could lead to a greater resistance to thermal degradation. The same authors showed that lignin degradation begins at around 400 °C. It can be seen from Fig. 2 that the acid-insoluble material of oak treated at the highest extent (280 °C, 5h), as a function of mass loss, deviated slightly from linearity. This could be due to the fact that carbohydrate degradation is increased at this temperature.

Untreated oak was found to have a natural extractive content of 7.66% (Table 3), which is similar to the natural extractive content of oak reported by Monties (1987). For untreated maritime pine, different extractive contents to that of the present study (5.36%) have been reported: i.e. 14.2% (Ballesteros et al. 2000) and 9.96% (Markussen et al. 2002). Maritime pine is generally rich in natural resins, comprising volatile substances (Rowell et al. 2005). The samples used in this study might have contained less resin than those studied in the literature.

Both maritime pine and pedunculate oak showed a similar variation in extractives content with treatment extent. At low treatment extent (mass loss below 6 %), the extractives content tended to increase, whereas at higher treatment extent (mass loss above 6%), the extractive content decreased (Table 3). Hakkou et al.

(2006) studied the heat treatment of beech wood and observed an increase of the extractive content for a mass loss below 20% and a decrease for a higher mass loss. According to Weiland and Guyonnet (2003) the increase of the extractive content is probably due to the onset of hemicelluloses degradation, which produces new extractible components. At high temperature levels, the decrease in extractive content would correspond to its thermal degradation.

Energy Properties

The volatile matter content, fixed carbon content, and higher heating value of the wood samples are presented in Table 4.

Table 4. Proximate Analyses and Higher Heating Value (HHV) of Maritime Pine and Oak Woods

Temperature (°C)	Time (h)	Proximate analysis					
		Volatile matter (%)		Fixed carbon (%)		HHV (MJ/kg)	
		M	SD	M	SD	M	SD
Maritime pine							
Untreated		79.0a	0.2	20.3a	0.3	20.0a	0.1
220	1	79.1a	0.2	20.4a	0.2	20.37b;c	0.04
220	5	81.0c	0.2	18.5c	0.1	20.2c	0.2
250	1	79.4a	0.2	20.1a	0.2	20.45b	0.03
250	5	77.5d	0.2	21.9d	0.2	20.84d	0.01
280	1	72.5b	1.8	27.2b	1.8	21.70e	0.03
280	5	65.5e	0.1	34.17e	0.01	23.07f	0.01
Pedunculate oak							
Untreated		79.6a	0.6	19.9a	0.8	19.26a	0.01
220	1	78.0b	-	21.3b	-	19.8b	0.1
220	5	77.4b	1.2	22.2b	1.2	19.94c	0.03
250	1	74.2c	0.1	25.3c	0.2	20.25d	0.01
250	5	62.3d	1.0	28.8d	1.1	20.79e	0.01
280	1	70.8e	1.1	37.0e	0.9	21.45f	0.03
280	5	50.7f	0.1	48.55f	0.01	22.71g	0.02

S.D. : Standard deviation (%) ; M: Means of duplicated sample; a : Means followed by the same letter are not significantly different (Tukey, α=5%)

As expected, the fixed carbon content increased with an increase in mass loss for both species. Such an increase implies that the torrefied biomass is suitable for energy production or for the use of charcoal as a reducing agent (pig iron industry).

The dimensionless fixed carbon content parameter indicates exactly how the heat treatment affected this characteristic in each species (Fig. 3). For example, when the sample lost about 22% of its mass, the dimensionless fixed carbon content was 1.3 for pine and 1.4 for oak.

The *HHV* (higher heating value) represents the maximum amount of energy embedded per kilo of a material. It is important to mention that *HHV* increases with the extent of treatment (Table 4). On the whole, Fig. 4 indicates that the dimensionless *HHV* increased linearly with an increase of mass loss in both species (R^2=0.94 for maritime pine and R^2=0.97 for oak wood).

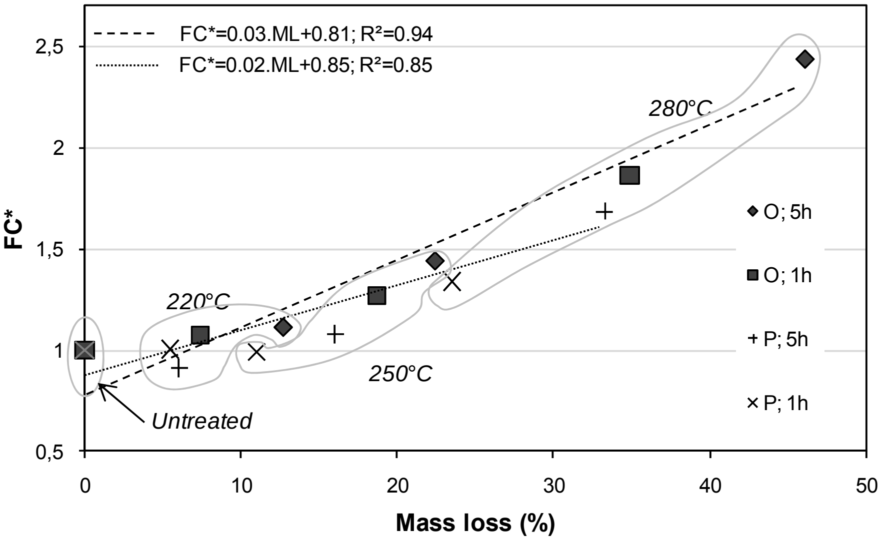


Fig. 3. Relative fixed carbon content (FC*) of untreated and heat-treated wood as a function of mass loss for maritime pine (P) and pedunculate oak (O). Data grouped in each circle were subjected to the same temperature of treatment.

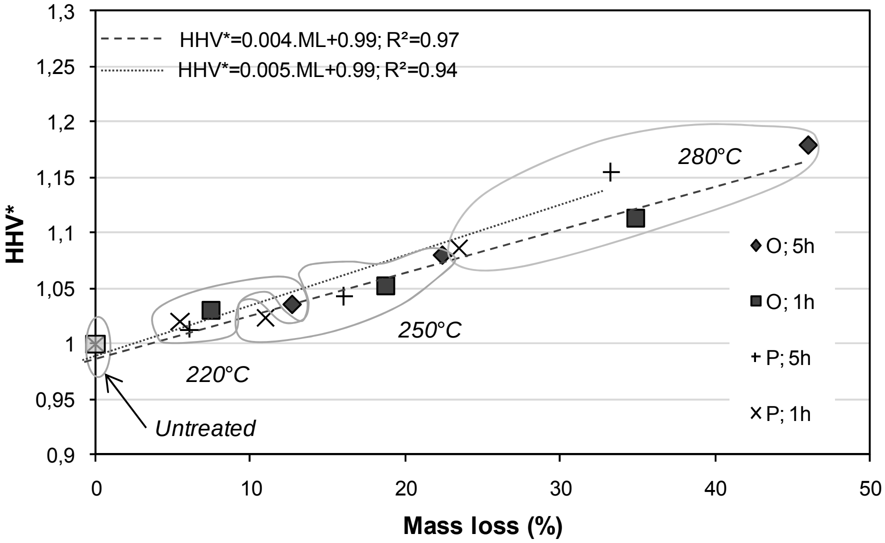


Fig. 4. Relative higher heating value (*HHV**) of untreated and heat-treated wood as a function of mass loss for maritime pine (P) and pedunculate oak (O). Data grouped in each circle were subjected to the same temperature of treatment.

As already observed for relative fixed carbon, the influence of heat treatment on *HHV** was similar in the two species. For example, for a mass loss of about 22%, the dimensionless *HHV** of maritime pine was 1.08, compared to 1.07 for oak. The correlation between fixed carbon content, volatile matter content and *HHV* (Demirbas 1997; Parikh 2005) shows that the same *HHV** variation was due to the same variations in fixed carbon and volatile matter content previously observed for the two species.

A good correlation was also found between *HHV* and acid-insoluble material content (Demirbas 2001):

$$HHV = 0.0893 \times AIM + 16.97 \qquad R^2 = 0.9658 \tag{6}$$

where *HHV* is the higher heating value (MJ/kg) and *AIM* is the acid-insoluble material content (%).

Figure 5 shows the *HHV* calculated from equation 6 as a function of the *HHV* measured.

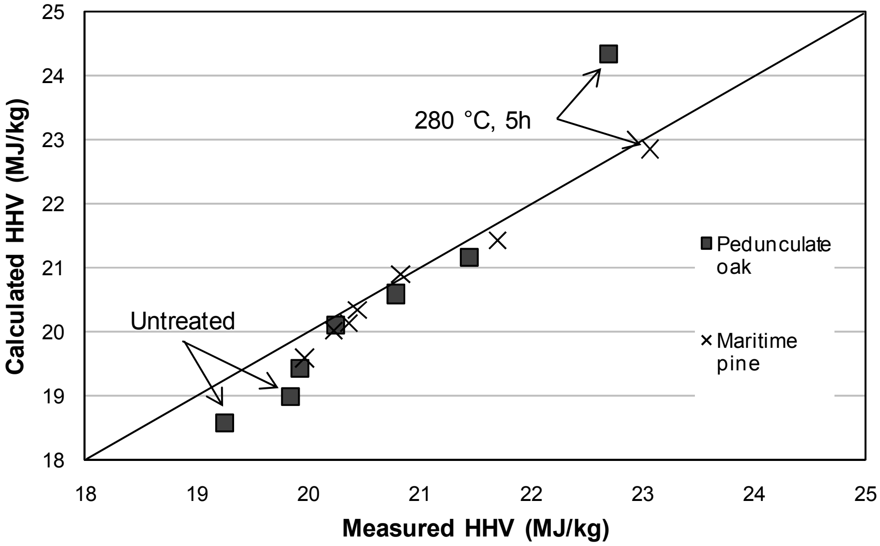


Fig. 5. HHV calculated according to Demirbas (2001) for maritime pine (P) and pedunculate oak (O) as a function of the measured HHV

On the whole, the results show that the calculated *HHV* was very close to the measured *HHV*, and the increase in *HHV* could be partially explained by the increased acid-insoluble material content. At lower treatment extents, the calculated *HHV* of oak was underestimated. The difference between the calculated and measured *HHV* was about 0.8 MJ/kg, which represents a difference of about 4 %. For oak treated under the most extreme condition (280 °C; 5h), the calculated *HHV* was higher than the measured *HHV*. As indicated in a previous paragraph, the acid-insoluble material content could be increased at the highest treatment extents by products derived from the thermal degradation of the carbohydrates, since hardwood hemicelluloses are more sensitive to heat than softwood ones. In this case, the calculated *HHV* for oak treated at 280 °C, 5 h was therefore overestimated.

Due to the increase of *HHV*, the decrease in energy yield with treatment extent was lower than the decrease in mass loss. For example, maritime pine treated at 280 °C for 5h lost 23% of its initial energy content compared to 33% of its initial mass loss. This difference seems to increase with the increase in the extent of treatment. Schenkel et al. (1997) reported a large range of energy yields of charcoal from different species and carbonization processes. In order to compare the energy yields resulting from torrefaction and carbonization processes, these data have been plotted in Fig. 6. The benefit of torrefaction relative to the energy concentration of biomass is clearly indicated.

The present study confirms the particular status of mass loss during the torrefaction process, while at the same time it is easy to determine and able to synthesize the cumulated effect of the two major treatment conditions, temperature and duration. To go further in this direction, simple linear regressions of several biomass properties are presented as a function of mass loss in Table 5.

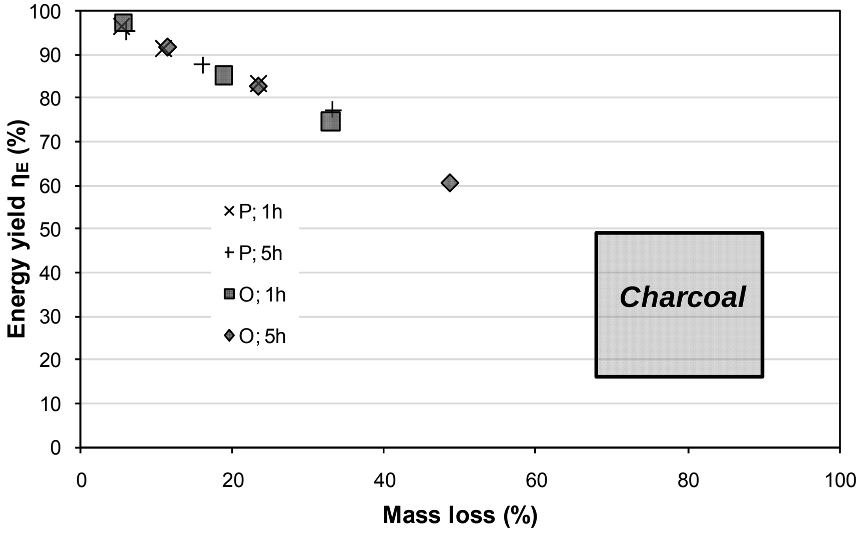


Fig. 6. Energy yield of maritime pine (P) and pedunculate oak (O) heat-treated under different conditions. Charcoal data comes from Schenkel et al. (1997)

Table 5. Linear Regressions of Biomass Properties as a Function of Loss (ML) due to Torrefaction

Properties	Linear regression	
Acid-insoluble material (AIM)	Maritime pine → $AIM = 27.99 \times (1 + 0.038\ ML)$	$R^2 = 0.97$
	Pedunculate oak → $LC = 13.66 \times (1 + 0.092\ ML)$	$R^2 = 0.94$
	Both species → $LC = 22.\ 18 \times (1 + 0.040\ ML)$	$R^2 = 0.84$
Fixed carbon (FC)	Maritime pine → $FC = 17.17 \times (1 + 0.026\ ML)$	$R^2 = 0.85$
	Pedunculate oak → $FC = 16.16 \times (1 + 0.039\ ML)$	$R^2 = 0.94$
	Both species → $FC = 16.17 \times (1 + 0.036\ ML)$	$R^2 = 0.90$
Higher heating value (HHV)	Maritime pine → $HHV = 19.71 \times (1 + 0.005.ML)$	$R^2 = 0.94$
	Pedunculate oak → $HHV = 19.14 \times (1 + 0.004\ ML)$	$R^2 = 0.97$
	Both species → $HHV = 19.58 \times (1+ 0.004\ ML)$	$R^2 = 0.79$
Energy yield (η_E)	Maritime pine → $\eta_E = 99.34 \times (1 - 0.007\ ML)$	$R^2 = 0.99$
	Pedunculate oak → $\eta_E = 101.07 \times (1- 0.008.ML)$	$R^2 = 1$
	Both species → $\eta_E = 100.59 \times (1- 0.008\ ML)$	$R^2 = 0.99$

CONCLUSIONS

This study investigated alterations in the chemical and energy characteristics of maritime pine and pedunculate oak woods subjected to different torrefaction conditions. The following main conclusions could be drawn from the results:

1. Acid-soluble material (ASM) was strongly affected within the range of temperatures studied. Thus, in the most severe treatment (280 °C, 5h), ASM content decreases more than 35% for pine and 60% for oak. In contrast, acid-insoluble material content increased, probably due to a side-effect of carbohydrate degradation.
2. Torrefaction increased the fixed carbon content and energy content of a given mass of the remaining material after treatment. These results are interesting for the use of biomass in energy production.
3. In the range of temperature and duration studied here, the dimensionless energetic properties obeyed the same functions of overall mass loss in both species.
4. The energy yield was always higher than the mass loss, the difference between these two parameters increasing with treatment extent. The comparison of torrefaction and carbonization processes revealed a better energy yield for torrefaction.

This study showed that mass loss is an excellent indicator of the extent of treatment. Therefore, all results have been summarized as analytical expressions able to predict the energy properties as a function of the overall mass loss within the range of temperatures and durations studied (220 to 280 °C; 1 to 5h). These expressions could be used in any decision-making process, including overall optimization of the transformation chain, from production in the field to the final usage.

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REFERENCES CITED

Almeida, G., Brito, J. O., and Perré, P. (2009). "Changes in wood-water relationship due to heat treatment assessed using micro-sample of *Eucalyptus*," *Holzforshung* 63(1), 80-88.

Almeida, G., Brito, J. O., and Perré, P. (2010). "Alterations of energy properties of eucalyptus wood and bark submitted to torrefaction: the potential of mass loss as a synthetic indicator," *Bioresource Technol.* 101, 9778-9784.

Agrawal, K. R. (1988). "Kinetics of reactions involved in pyrolysis of cellulose. I. The three reaction model," *Canadian J. Chem. Eng.* 66, 403-412.

Associação Brasileira de Normas Técnicas (ABNT). (1986). “Carvão vegetal – Análise imediata,” NBR 8112.

ASTM Standard. D5865. (2007). “A standard test method for gross calorific value of coal and coke,” ASTM International, West Conshohocken, PA, DOI: 10.1520/ D5865-07.

Avat, F. (1993). “Contribution à l’étude des traitements thermiques du bois (20-300°C): Transformations chimiques et caractérisations physico-chimiques,” Ph-D Thesis, Ecole Nationale Supérieure des Mines de Paris et Ecole Nationale Supérieure des Mines de Saint-Etienne.

Ballesteros, I., Olivia, J. M., Navarro, A. A., Gonzalez, A., Carrasco, J., and Ballesteros, M. (2000). “Effect of chip size on steam explosion pretreatment of softwood,” *Applied Biochemistry and Biotechnology* 84-86, 97-109.

Bekta, P., and Niemz, P. (2003). “Effect of high temperature on the change colour, dimensional stability and mechanical properties of spruce wood,” *Holzforshung* 57, 539-546.

Bergman, P. C. A., Boersma, A. R., Kiel, J. H. A., Prins, M. J., Ptasinski, K. J., and Janssen, F. J. J. G. (2005). “Torrefaction for entrained-flow gasification of biomass,” *Report ECN-C-05-067,* The Netherlands. 50 pp.

Bourgeois, J. P. (1989). “Thermocondensed lignocelluloses material, and a method and an oven for obtaining it,” *US Patent* 4,816,572.

Brito, J. O., Silva, F.G., Leão, M. M., and Almeida, G. (2008). “Chemical composition changes in eucalyptus and pinus woods submitted to heat treatment,” *Bioresource Technol.* 99, 8545-8548.

Carvalho, A. (1960). “Alguns inconvenientes do azulamento na madeira de *P. Pinaster* com vista ao seu aproveitamento em pasta para papel,” *Separata das publicações da Direcção Geral dos Serviços Florestais e Aquicolas* 27.

Colin, J. (2007). “Etude de la pyrolyse ménagée du bois: Mise au point d‘un four de traitement thermique, essais expérimentaux et utilisation d’un code numérique de simulation,” Master Thesis, Université Henri Poincaré, Nancy 1 et AgroParisTech ENGREF.

Demirbas, A. (1997). “Calculation of higher heating values of biomass fuels,” *Fuel* 76(5), 431-434.

Demirbas, A. (2001). “Relationship between lignin contents and heating values of biomass,” *Energy Conversion and Management* 42, 183-188.

Esteves, B., Velez Marques, A., Domingos, I., and Pereira, H. (2007). “Influence of steam heating on the properties of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) wood,” *Wood Sciences and Technology* 41, 193-207.

Govin, A., Repellin, V., Guyonnet, R., Rolland, M., and Duplan, J. L. (2009). “Effect of torrefaction on grinding energy requirement for thin wood particle production,” *Récents Progrès en Genie des Procédés* 98, 756(1)-756(6).

Hakkou, M., Pétrissans, M., Gérardin, P., and Zoulalian, A. (2006). “Investigations of the reasons for fungal durability of heat-treated beech wood,” *Polymer Degradation and Stability* 91, 393-397.

Kamdem, D. P., Pizzi, A., and Jermannaud, A. (2002). “Durability of heat-treated wood,” *Holz als Roh und Werkstoff* 60, 1-6.

Kollman, F., and Fengel, D. (1965). “Changes in the chemical composition of wood by thermal treatment,” *Holz als Roh und Werkstoff* 23, 461-468.

Markussen, T., Fladung, M., Achere, V., Favre, J. M., Faivre-Rampant, P., Aragones, A., Da Silva Perez, D., Harvengt, L., Espinel, S., and Ritter, E. (2002).

"Identification of QTLs controlling growth, chemical and physical wood property traits in *Pinus pinaster* (Ait.)," *Silvae Genetica* 52(1), 8-15.

Monties, B. (1987). "Composition chimique du bois de chêne: Composés phénoliques, relations avec quelques propriétés physiques et chimiques susceptibles d'influencer la qualité des vins et des eaux-de-vie," *Connaissances de la Vigne et du Vin* 21, 169-190.

Parikh, J., Channiwala, S. A., and Ghosal, G. K. (2005). "A correlation for calculating HHV from proximate analyses of solid fuels," *Fuel* 84, 487-494.

Repelin, V. (2006). "Optimisation des parameters durée et temperature d'un traitement thermique du bois. Modifications des proprieties d'usage du bois en relation avec les modifications physico-chimiques et ultrastructurales occasionnées par le traitement thermique," Ph-D Thesis, Ecole nationale supérieure des mines de Saint-Etienne et Université Jean Monnet de Saint-Etienne.

Rousset, P., Turner, I., Donnot, A., and Perré P. (2006). "Choix d'un modèle de pyrolyse ménagée du bois à l'échelle de la micro-particule en vue de la modélisation macroscopique, " *Annals of Forest Sci*. 63, 213-229.

Rowell, R. M. (2005). "Chemical modification of wood," *Handbook of Engineering Biopolymers,* Hanser Publisher, Munich, 674-691.

SAS Institute. (2002) SAS 9.0 Ed. SAS Institute, Inc., Cary, NC.

Sivonem, H., Maunu, S., Sundholm, F., Jämsä, F., and Viitiameni, P. (2002). "Magnetic resonnance studies of thermally modified wood," *Holzforschung* 56, 648-654.

Schenkel, Y., Bertaux, P., Vanwijnsberghe, S., and Carré, J. (1997). "Une évaluation de la technique de la carbonisation en meule," *Biotechnol. Agron. Soc. Environ.* 1, 113-124.

TAPPI standard (1994). T 204. OM-88, "Acid-insoluble lignin in wood and pulp."

TAPPI standard (1994). T 204. OM-88, "Solvent extractives of wood and pulp."

Tjeerdsman, B., Boonstra, M., Pizzi, A., Tekely, P., and Militz, H. (1998). "Characterisation of thermally modified wood: Molecular reasons for wood performance improvement," *Holz Roh-Werkst* 63, 102-111.

Thomas, R. J. (1977). "Wood: Structure and chemical composition," *ACS Symposium Series* 43, 1-23.

Turner, I. W., Rousset, P., Rémond, R., and Perré P. (2010). "An experimental and theoretical investigation of the thermal treatment of wood in the range 200-260°C," *Int. J. Heat Mass Transfer* 53,715-725.

Unsal, O., and Ayrilmis, N. (2005). "Variations in compression strength and surface roughness of heat-treated Turkish river red gum (*Eucalyptus camaldulensis*) wood," *Journal of Wood Science* 51, 405-409.

Weiland, J. J., and Guyonnet, R. (2003). Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy," *Holz als Roh-und Werkstoff* 61, 216-220.

Yildiz, S., Gezer, E. D., and Yildiz, U. C. (2005). "Mechanical and chemical behavior of spruce wood modified by heat," *Building and Environment* 41, 1762-1766.

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