Measurement of Gaseous and Particulate Pollutants during Combustion of Date Palm Wastes for Energy Recovery

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ABSTRACT

Being an important date-producing country, Tunisia generates high quantities of dry date palm residues which are currently not efficiently used, and instead accumulate every year in oasis lands. These by-products could present real advantages for Tunisia for energy production in both economic and environmental terms. Heating installations using biomass generate primary pollutants, such as CO, VOC and Particle Matter (PM), these latter having the most important adverse impact on environment. Measurements of these pollutants are needed, because international certification organizations require drastic limits on CO and PM emissions from biomass combustion processes.

In this study, date palm leaflets (DPL), date palm rachis (DPR), date palm trunks (DPT) and date stones (DS) were combusted in a laboratory scale mobile furnace. The aim of this work was to find an appropriate of these materials for energy recovery, with low emission factors of gaseous and PM in the exhaust. Combustion tests were performed at two temperatures (500°C and 800°C) and input air flow rates (25 and 50 NL/h). With the lowest content of chlorine and the highest bulk and energetic densities, DS is the most convenient date palm residue for energy recovery. Combustion of DPL, DPR and DPT needs to be performed at high temperature to obtain a complete carbon balance, and this is not required for the combustion of DS, which has a value of 88% for the carbon balance at 500°C.

Particles emitted during combustion are mainly constituted of fine and ultrafine particles. For all samples, 99% are particles with diameters below 1 μm. Combustion of DS produces the lowest content of $PM_{0.1}$, leads to the lowest emissions factors of aerosols, and generates fewer tars than the other date palm by-products. An increase in the input air flow rate, and therefore decrease in the residence time during combustion of DS, generates a larger amount of aerosols.

Keywords: Thermal oxidation; Date palm waste; Gas release; Emission factor; Aerosols.

INTRODUCTION

An attractive aspect of biomass utilization is its renewability, which ultimately guarantees that the sources will not be depleted. With plant and plant-derived materials, all energy is originally captured by photosynthesis (Lee *et al.*, 2007). In particular, utilization of agricultural residues as an energy resource has various economic and environmental advantages, and may be a promising solution to the problems of rising energy demand and finite supplies of fossil fuels, as it does not affect with the production or cost of foods.

Tunisia, like many other developing countries, needs to identify and exploit all their available energy resources with the goal of achieving sustainable development. Although Tunisia does not produce oil, it has significant reserves of renewable energy that are currently not being used, such as solar energy and biomass derived fuels. The main sources of biomass include agricultural residues, such as olive and date palm waste. These lignocellulosic materials are available in large quantities, and their use does not compromise food crops.

The date palm (Phoenix dactylifera) is one of the most cultivated palms in arid and semi-arid regions (Fig. 1), and about 105 million date palms are currently being grown around the world (Agoudjil *et al.*, 2011). The global production of dates has seen considerable expansion over the last decade, rising from 6,542,760 tons in 2004 to 7,429,811 tons in 2009 (Foastat, 2010), and expanding fruit production has naturally resulted in increased amounts of waste every year. Tunisia has approximately 4.5 million date trees, covering an area of 32,000 ha (Rhouma, 2005),

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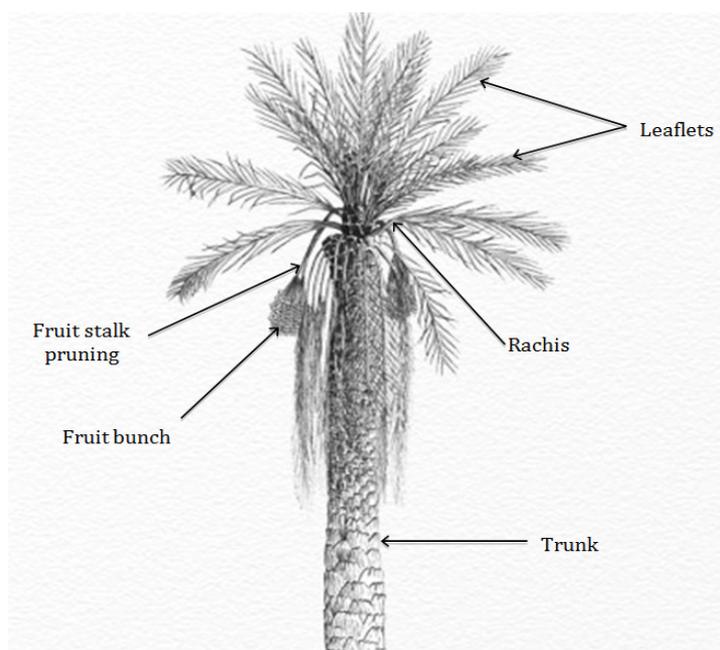 *E-mail address:* gwenaelle.trouve@uha.fr

Fig. 1. Date palm tree.

and is currently among the top 10 world producers of dates and the first exporter in value. In recent years, Tunisian production has reached an annual average of 145,000 tons, dominated by the Deglet Nour variety, which accounts for about 60% of the total production. This variety is prized for its taste, and has a high commercial value. Significant amounts of date palm by-products are produced during harvesting, such as leaves, fruitstalk prunings, fruit wastes and date stones. For example, the date stones represent about 10% of the weight of the fruit (Haimour *et al.*, 2006), while 198,000 tons of leaves are produced each year in Tunisia (Bchini *et al.*, 2002). In addition, tree trunks also become available for reuse upon natural or accidental death of the palm, or by forced removal. Therefore, a vast amount of date-related waste is produced, and finding more effective ways to use it is of obvious interest.

Date palm residues already have many applications, such as paper pulp production, fibers for composite materials, and the preparation of activated carbon (El Morsy, 1980; Barreveld, 1993; Haimour *et al.*, 2006; Bouchelta *et al.*, 2008; Khiari *et al.*, 2010). Nevertheless, few studies evaluated the use of date palm by-products as a renewable energy source. Al-Omari (2006, 2009) examined the conversion of date stones and palm stalks to thermal energy via combustion at different experimental conditions in a small scale furnace with a conical solid fuel bed. The results were presented as functions of time for the mass of solid fuel in the bed, the rate of change of this mass due to fuel addition and fuel combustion, the temperatures at the top of the fuel bed and at the furnace exit, and the rate of heat transfer to the cooling water jacket. For a date stone feed rate of about 100 g/s, the rate of heat transfer to the cooling water was about 10 kW. The author noted that these biomasses are a technically viable alternative fuel in heat generation installations. Comparisons with coal under the same conditions showed that date stones contain much more levels of volatile compounds as coal, and with sufficiently high amounts of air the heat transfer rates per unit mass of date stone are in the same order of magnitude as those of coal (Al-Omari, 2006).

Gas emissions analysis is very important with regard to thermal treatment of waste, due to the stringent standards on CO, VOC and particulates emissions imposed by European regulations. Even if gaseous emissions are well controlled, particle emissions still need to be carefully monitored. This is especially true for ultrafine particles, with diameters below 1 μm, as these get deposited in the alveolar regions of the lung, where the absorption efficiency for trace elements is up to 60–80% (Linlay *et al.*, 1997; Becker *et al.*, 2005). Therefore, in a context of environmental policy, it is also of considerable interest to identify and characterize the sources of ultrafine particles.

Due to their high volatile mineral content, in particular alkali metal salts, many biomasses are a significant source of particulate pollutants, such as fine and ultrafine particles during combustion. Numerous studies have undertaken the characterization and quantification of aerosols formed during biomass combustion at different scales (Christensen *et al.*, 1997; Obernberger *et al.*, 1997; Valmari *et al.*, 1997; Jiménez *et al.*, 2005; Ehrlich *et al.*, 2007; Tissari *et al.*, 2007; Hindiyarti *et al.*, 2008; Sippula *et al.*, 2008). The results of these works reveal the important role of the chemical composition of biomass, particularly the potassium, sulfur and chlorine contents, in the amount of fine particles generated during combustion. These elements are well volatilized during the combustion process and nucleate/ condense in fine particles (with diameter < 1 μm) during the cooling of flue gas (Christensen *et al.*, 1997; Jiménez *et al.*, 2005). Jenkins *et al.* (1998) and Sippula *et al.* (2008) showed that an increase in the chlorine content of

the biomass being burned leads to an increase in the amount of fine particles emitted during combustion. Ultrafine particles (with diameter > 1 μm) come from the non-vaporization of ash species in biomass, and the condensation of tars and oils.

Cascade impactors are widely used for the study of particulate matter produced during combustion, since they allow for the collection of particles and the assessment of their size distribution. Consequently, they are now widely used to examine the particles emitted from wood combustion sources (Christensen *et al.*, 1997; Valmari *et al.*, 1997; Johansson *et al.*, 2003; Jiménez *et al.,* 2005; Wierzbicka *et al.*, 2005; Ehrlich *et al.*, 2007; Tissari *et al.*, 2007; Wiinikka *et al.*, 2007; Sippula *et al.*, 2008; Zhang *et al.*, 2011).

While date palm residues may be used as an energy source, more information is needed with regard to the related emissions factors of gaseous and particulate pollutants, so that this process can comply with regulatory standards. The aims of this paper are thus first to select the most suitable date palm residues for combustion, based on their thermal and chemical properties. The second aim is the measurements of both emission rates and factors of the main gases, namely the carbon oxides and volatile organic compounds, as well as the fine and ultrafine particles in the fumes.

METHODS

Sample Preparation

Date palm residues were provided from different varieties of date palm accumulated in the south of Tunisia, and dried under natural conditions over 2–3 days, in order to remove water. The date palm leaflets (DPL) were separated manually from the rachis and cut to 1–2 mm in width and 4–5 mm in length. Date palm rachis (DPR), date-stones (DS), and date palm trunks (DPT) were ground separately in order to have homogeneous products. After sieving, one common particle size, ranging from 1 to 2 mm, was selected for each of the five samples for the subsequent combustion tests.

Physical and Chemical Characterization of Samples

In order to obtain the properties of the biomass materials related to their thermo-chemical conversion, standard test methods, namely proximate and ultimate analyses, were performed. Besides, the heating values were measured using an adiabatic oxygen bomb calorimeter from REKA.

Combustion Tests

The experimental set-up used for the combustion of the samples under fixed-bed conditions is shown in Fig. 2. It basically consists of a vertical fused silica reactor with a fused silica frit (16 mm in diameter), and a heating system equipped with a mobile ceramic furnace. Samples of biomass (20 to 150 mg) were placed on the frit while positioned outside the ceramic furnace under air flow (at different gas flow rates: 25 and 50 NL/h). The furnace was then heating until the set-point temperature. Two temperatures were tested (500°C and 800°C). During this period, the bed temperature, measured using a thermocouple located 1 mm above the sample, was maintained at ambient temperature
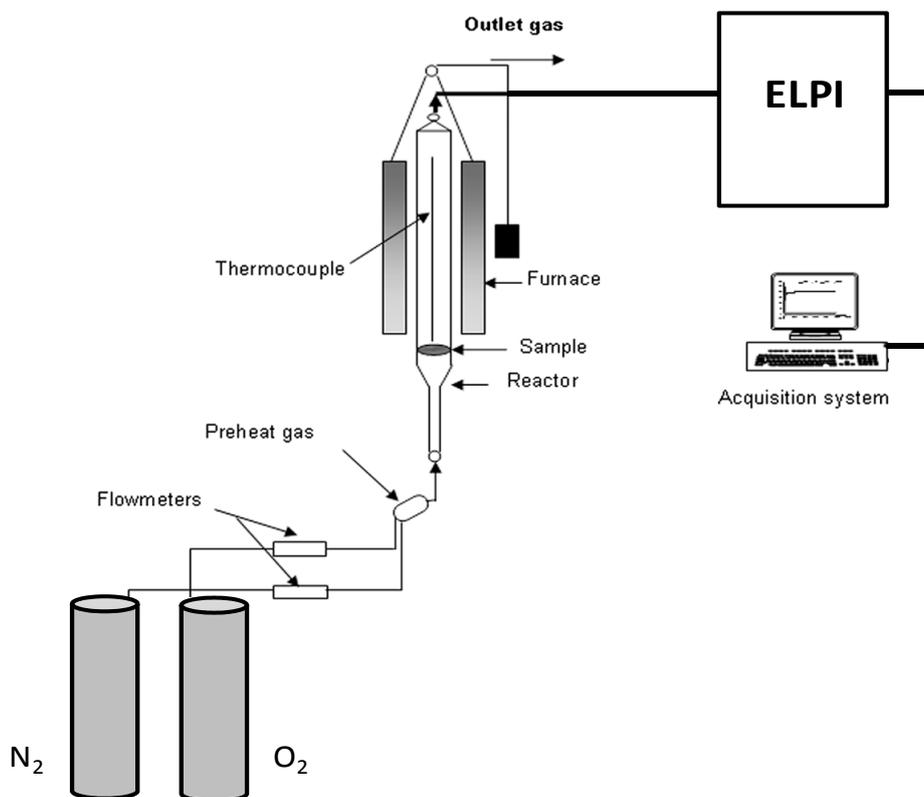

Fig. 2. Experimental device for combustion of date palm residues.

using a cooling system. Once the set-point temperature was reached, the furnace was rapidly moved down in order to introduce the sample into the heating zone of the tubular furnace. The device also includes a gas cleaner (glass wool filter, dust filter) and a gas dryer before the analyzers. The emissions were characterized using online gas analyzers. Immediately after leaving the reactor, part of the exhaust gas flow was aspirated toward a flame ionization detector (COSMA graphite 655: range 1–10000 ppm) to quantify the volatile organic compounds. After being dried and cleaned, the rest of the exhaust gas flow passed through a set of analyzers, where mole fractions of CO_2 and CO were measured by Rosemont infrared analyzers (BINOS 100 for CO and CO_2: range 0–6% and 0–10%, respectively).

Aerosol Measurements

Aerosol emissions in the gas phase were recorded every 2 s with an Electrical Low Pressure Impactor from DEKATI. This cascade impactor separated the particles based on the aerodynamic equivalent cut-off diameter (Dae), in twelve size fractions ranging from 28 nm to 10 μm. The twelve impaction stages were warmed at 110°C in order to avoid water condensation. At the end of combustion, the warmed furnace was moved to its original position to recover emissions of tars deposited on the cold top of the reactor during combustion. Small masses of about 20 mg of the date palm waste (DPW) sample were combusted to record the particle emissions. Under these conditions, dilution of the particle flow at the entrance of the ELPI was not necessary.

RESULTS AND DISCUSSION

Physical and Chemical Characterization of Samples

In order to assess the utilization of date palm residues as an effective source of renewable energy, it is necessary to investigate the specific properties that determine their performance as a fuel in combustion. The results of the proximate and ultimate analyses, along with bulk densities, are given in Table 1. Compared with the data in the literature concerning wood biomass and energetic crops, these date palm residues have typical compositions (Senneca *et al.*, 2007; Chouchene *et al.*, 2010; Jeguirim *et al.*, 2010; Verma *et al.*, 2012). However, the chlorine content appears to be very high in comparison with commercial agro-pellets and standardized wood pellets, such as DIN+, particularly for the DPR and DPT samples, with values above 1% (Verma *et al.*, 2012). This indicates that this element in the gas and particles of the fumes needs to be controlled in order to reduce both the corrosion impacts and emission factors of persistent organic pollutants, such as dioxins and furans (Schatowitz *et al.*, 1994; Lavric *et al.*, 2004). Low heating values (LHV) are seen for the samples, in intervals ranging from 15.2 to 19.0 MJ/kg. The results show that the samples have high energy potential, in the same order of magnitude as the results obtained for olive solid waste, Miscanthus, wood pellets and wood chips (Senneca *et al.*, 2007; Chouchene *et al.*, 2010; Jeguirim *et al.*, 2010; Verma *et al.*, 2012). Among various date palm residues, the DS sample, which has the highest percentage of volatiles (VM) and fixed carbon (FC), and the lowest ash and chlorine contents, presents the highest calorific value in term of LHV. Large differences are observed among the samples for the amounts of humidity and ash, and this may explain the variations in the LHV values. Moreover, an important characteristic of biomass materials is their bulk density, which is a factor in the related transport and storage costs. The bulk density of DS is relatively high (656 kg/m³), close to that of wood chips (550 kg/m³) and wood pellets (693 kg/m³) (Senneca *et al.*, 2007; Verma *et al.*, 2012). Both the heating value and bulk density establish the energetic density, which is the potential energy available per unit of biomass. Table 1 shows that the values of energetic density show the same trend as those of bulk density. DS energetic density, close to the one of wood pellets (12 GJ/m³) is much higher than the remained samples Furthermore, it is nearly

Table 1. Proximate and ultimate analyses of DPW.

Biomass samples	DPL	DPR	DPT	DS
Proximate analysis[a]				
Moisture (%)	7.1	12.1	10.0	6.4
Volatile Matter (%)	68.0	73.6	71.8	74.1
Fixed Carbon (%)	9.7	8.3	11.5	17.5
Ash (%)	15.2	6.0	4.2	1.2
Low Heating Value (MJ/kg)[b]	19.0	15.2	15.5	17.4
Bulk density (kg/m³)	312	173	213	656
Energetic density (GJ/m³)[b]	5.9	2.6	3.3	11.4
Ultimate analysis[a]				
C (%)	40.8	39.8	42.8	51.2
H (%)	6.0	5.7	5.8	6.4
O (%)	35.2	43.0	45.5	40.9
N (%)	0.63	0.19	0.21	0.73
S (%)	0.21	0.26	0.12	< 0.20
Cl (%)	0.52	3.51	1.07	0.0830

[a] Calculated on wet basis
[b] calculated based on dry free ash

double of the energetic density of wood chips, which is 6.4 GJ/m^3 (Senneca *et al.*, 2007; Verma *et al.*, 2012). With regards to both chemical and physical properties, DS seems to be the most attractive of the date palm wastes examined in this work, for energy production and low cost transportation.

Emissions of Main Gaseous Pollutants

Combustion of 150 mg of DPL, DPR, DPT and DS were performed in the experimental device shown in Fig. 2 at 500°C and 800°C under an air flow rate of 50 NL/h. Carbon oxides (CO and CO_2) and VOC were measured online. Two experiments for each sample were repeated at all temperatures. These experiments are a preliminary study in order to compare the thermal behaviors of these materials with those of energetic crops and biomasses previously described in literature. The emission rates of CO_2 for all DPW at 500°C versus the time are given in Fig. 3. Total carbon emission rates for CO, CO_2 and VOC are shown in the Fig. 4 for DS at 500°C and 800°C. The initial time (t = 0 s) corresponds to the moment when the furnace was moved down in order to place the date sample in the heating zone. A delay of 40 s was needed to observe the ignition of DPL, DPR and DPT, while DS combustion needed much more longer to (180 s). To further investigate the combustion behaviour of the DPW samples, an ignition index (D) was developed based on the following equation:

$$D = \frac{R_{max}}{(t_m t_i)} \quad (1)$$

where R_{max} is the maximum emission rate of CO_2, and t_m and t_i are the times corresponding to the maximum emission rate of CO_2 and ignition temperature, respectively. In the literature, the ignition index is generally calculated

according TGA, where R_{max} is defined as the maximum mass loss rate (Vamvuka and Sfakiotakis, 2011). Values for R_{max}, t_m, t_i and D are given in Table 2. Parameter t_f, corresponding to the end of the combustion process, is also presented in Table 2. Both t_i and t_m significantly decrease when the temperature increases from 500°C to 800°C for all DPW samples. The reactivity is increased with the temperature for all samples, as seen in Table 2 by the comparison of D values at both temperatures. The values of D significantly increase with as the temperature rises. At a relatively low temperature of 500°C, a comparison of the D values reveals an important difference in the thermal behaviour of these samples. Fibrous materials having a low bulk density, as DPL, DPR and DPT show similar values of D, close to 0.02. These values are one order of magnitude higher than that of DS, which has a much higher bulk density at the same temperature, as previously noted by Khalfi *et al.* (2004). The ignition time depends on material properties as thermal conductivity, bulk density and specific heat, and the different ignition times observed for the fibrous and DS samples significantly affected the thermal behaviors of these materials (Khalfi *et al.*, 2004). Fibrous materials do not have the same thermal ignition properties at 800°C, with different D values ranging from 0.018 to 0.081. At this temperature, the reactivity of DS does not differ from other samples, with a D value in the same order of magnitude, and very close to that of DPT.

Total carbon emitted in the forms of CO_2, CO and VOC (expressed by grams of date palm residue) and the molar ratios nCO/nC$_{Total}$ and nVOC/nC$_{Total}$ are given in Table 3 for all samples at 500°C and 800°C. The thermal oxidation of these samples does not proceed via complete reaction, and instead occurs with the formation of significant amounts of carbon monoxide and volatile organic compounds. A high temperature (800°C) is necessary to achieve complete
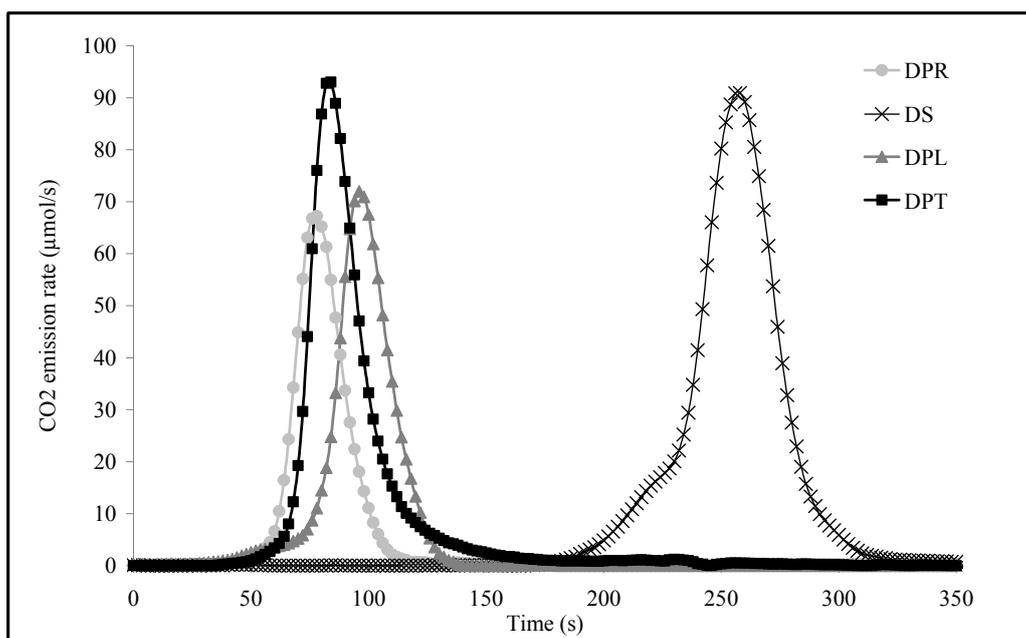

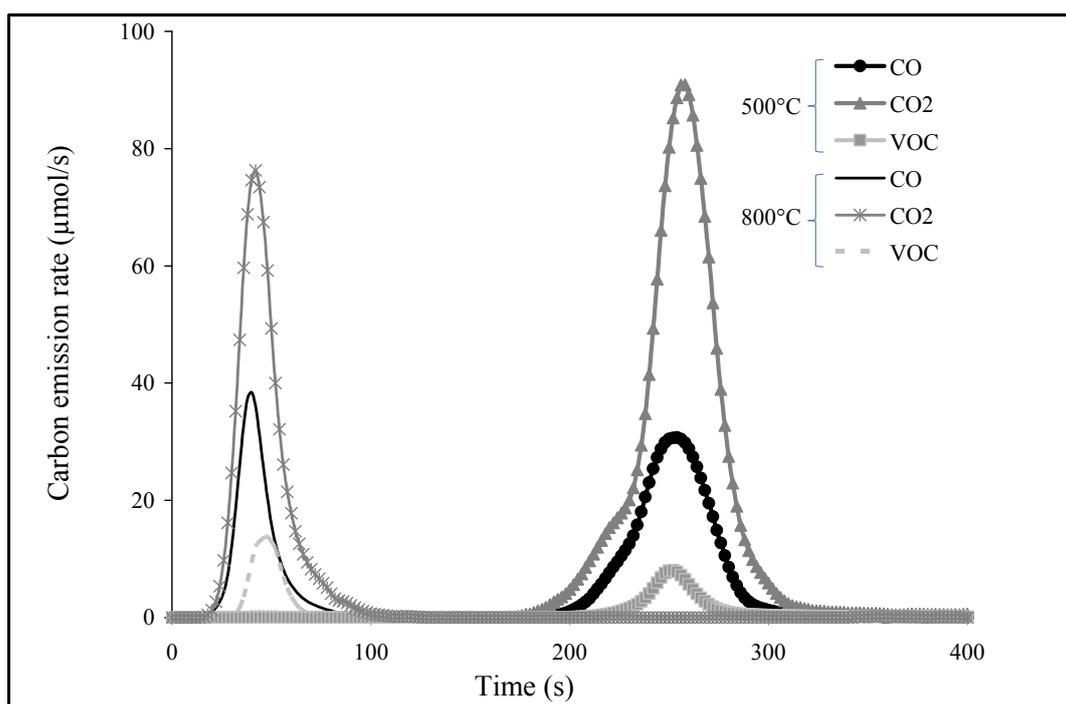**Fig. 3.** Emission rates of CO_2 for DPW at 500°C.

Fig. 4. Emission rates of carbon (CO, CO_2 and VOC) for DS at 500°C and 800°C.

Table 2. Characteristic combustion parameters of samples.

Biomass samples	DPL	DPR	DPT	DS
500°C				
t_i (s)	38	44	50	184
t_{max} (s)	96	78	84	258
t_f (s)	144	130	238	340
R_{CO2max} (μmol/s)	72.0	67.3	93.0	90.9
R_{COmax} (μmol/s)	18.3	49.5	68.7	30.7
R_{VOCmax} (μmol/s)	10.9	11.5	07.1	08.1
D	0.019	0.019	0.020	0.002
800°C				
t_i (s)	26	38	18	20
t_{max} (s)	48	62	38	42
t_f (s)	82	116	102	102
R_{CO2max} (μmol/s)	61.2	46.7	57.5	76.3
R_{COmax} (μmol/s)	60.7	36.6	60.3	38.4
R_{VOCmax} (μmol/s)	9.7	9.8	12.2	12.4
D	0.049	0.019	0.081	0.090

Table 3. Total carbon and molar ratios at different temperatures.

Biomass samples	DPL	DPR	DPT	DS
500°C				
Total $C_{(CO2+CO+VOC)}$ (mmol/g)	19.5	22.8	28.4	37.5
Total C (%)	57	69	80	88
nCO/nC_{Total}	0.17	0.36	0.33	0.25
$nVOC/nC_{Total}$	0.14	0.10	0.05	0.06
800 C				
Total $C_{(CO2+CO+VOC)}$ (mmol/g)	32.6	27.7	32.3	36.3
Total C (%)	96	84	91	85
nCO/nC_{Total}	0.41	0.39	0.44	0.27
$nVOC/nC_{Total}$	0.07	0.11	0.09	0.09

thermal oxidation. At 800°C, carbon total values expressed in mmol per gram of residue represent 96%, 84% and 91% for DPL, DPR and DPT of the initial carbon content in these DPW, respectively. DS is not really affected by an increase in temperature, and its combustion at the lower temperature of 500°C gives a total carbon emission factor of 37.5 mmol/g, representing 88% of the initial carbon content present in this residue. The carbon balance sheet at 800°C for DS represents 85% of the initial carbon. The differences in $nCO/nCtot$, $nVOC/nCtot$ and Total C for the two temperatures for DS are not significant, because they are in the order of relative standard deviation. An increase in the temperature particularly influences the emission

factor of CO for all the DPW, except for DS. This behaviour was previously described by Khalfi *et al.* (2000, 2004) during combustion tests of both natural fibers of wood pulp and boards of natural wood pulp in a laboratory device at temperatures ranging from 800°C to 1077°C. Khalfi *et al.* (2000, 2004) demonstrated that the bulk density of the sample is a very important factor, and those with a high bulk density, such as boards of wood pulp, underwent complete combustion, with traces of CO being detected in the emissions. In case of samples with a low bulk density, such as wood pulp, an increase in CO emissions was also observed with the rise in temperature. A comparison of the molar ratios of nCO/nCO_2 at 800°C obtained in this work with those in Khalfi *et al.* (2000) shows that samples with a high bulk density, such as DS and boards of natural wood pulp, have lower values than fibrous materials, such as natural wood pulp and DPL, DPR and DPT. As mentioned above, heat transfer into the

materials is also dependent of the form of the residue. If the bulk density may explain the different behaviors of fibrous and dense materials with regard to temperature in both the current and earlier studies, then there may be an additional explanation for this. The molar ratios of nCO/nCO_2 for natural wood board and natural wood pulp were 0.02 and 0.3 at 800°C, respectively, in Khalfi *et al.* (2004), while the values were 0.45 for DS and ranged from 0.77 to 0.91 for DPR, DPL and DPT. The residence time of gases in this earlier study's device was 2.4 s, whereas it was 0.3 and 0.2 s at 500°C and 800°C, respectively, in the present work. These very short times do not allow for good mixing of volatiles with oxygen during the tests, and thus oxygen diffusion may be difficult, and this could explain the high emissions of CO during our combustion tests.

Emissions of Fine and Ultrafine Particles

Measurements of fine and ultrafine particles were recorded during the combustion at 800°C under air at a flow rate of 50 NL/h for all samples. This temperature was chosen because it allowed the best carbon balances. Both influences of the temperature (500–800°C) and the air flow rate (25–50 NL/h) were only examined for the DS sample, because this by-product showed the best thermal properties. Fig. 5 gives the emission rates of particles versus the time for all DPW samples at 800°C. Because the ELPI apparatus was operated at a very high flow rate of 600 NL/h and had a short response time of 1 s, the particulate pollutants generated during combustion tests were recorded in real time, and aerosols were emitted after 20 s. According to Fig. 5, two peaks of particle matter occurred during the combustion tests before 500 s, which indicate that combustion proceeded in two clear steps. The first step corresponds to the removal of the volatile matter, which leads to the formation of char, while the second step

corresponds to the oxidation of this char. The emission of aerosols during the combustion of DS is fast and complete in 160 s. For the fibrous materials, namely DPR, DPT and DPL, an additional peak is observed at 700 s, 1100 s and 1200 s, respectively. This corresponds to the particles of tars being deposited on the cold part at the top of the reactor during the combustion test. These tars were subjected to a high temperature at the end of the test, when the warm furnace was returned to its original position at the top of the reactor. They were then devolatilized and detected by the ELPI. No additional peak is observed for DS, and the thermal oxidation of this by-product is more complete than that of the other DPW, and thus does not generate tars.

Number size distributions of PM_{10} for DPW at 800°C are given in Fig. 6. The four palm waste residues show similar number size distributions, with the $PM_{0.1}$ fraction being the dominant one. The total number of particles (which includes particles of tars detected after combustion test and corresponding to the third peak of aerosols) and the relative proportions of four different size fractions ($PM_{0.1}$; $PM_{0.1-1}$; $PM_{1-2.5}$; $PM_{2.5-10}$) are given in Table 4. Combustion of these palm date residues mainly leads to the formation of fine and ultrafine particles with diameters below 1 μm in the exhaust. The PM_1 size fraction represents more than 99% of the total number of particles emitted during the combustion test. Combustion of DS (which is characterized by greater energetic density) generates the lowest aerosol emissions, with a total number of PM_1 equal to 10×10^{12} particles per gram of biomass, whereas for DPL, DPR, and DPT, the total number of PM_1 reaches 16×10^{12}, 45×10^{12}, and 54×10^{12} particles per gram of biomass, respectively. The proportion of ultrafine particles is high for all DPW, accounting for more than 72% of the total number of particles emitted during combustion tests. This corresponds to 7.2×10^{12} particles per gram of biomass for
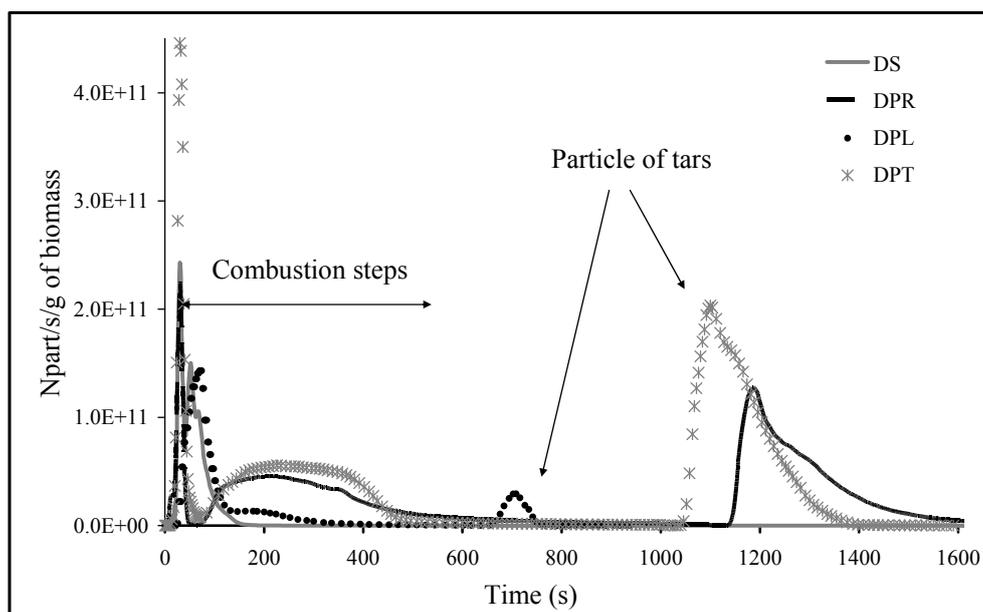

Fig. 5. Particle number emission rates as function of time during DPW combustions at 800°C.
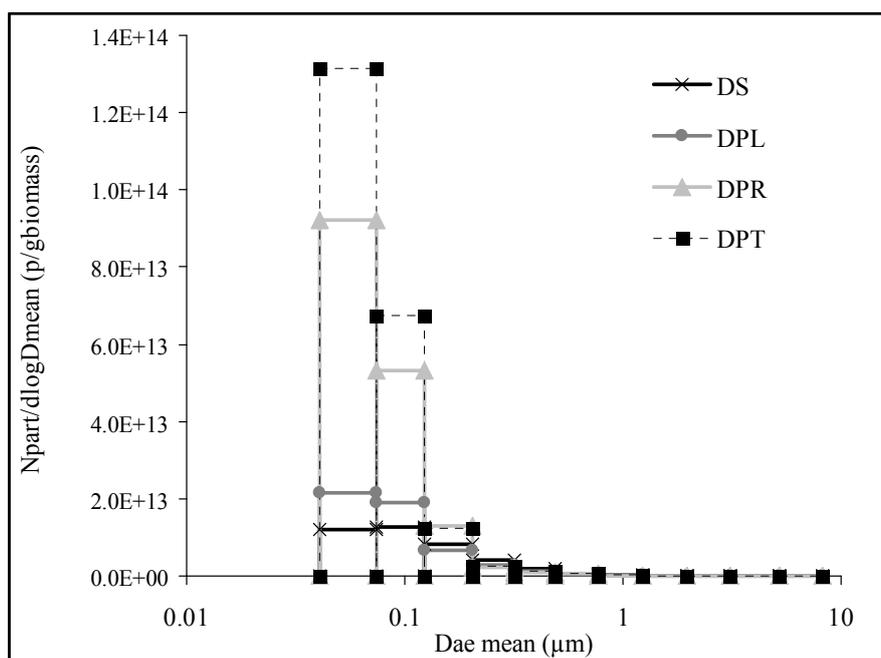
Fig. 6. Number size distributions of PM_{10} for DPW at 800°C under an air flow rate of 50 NL/h.

Table 4. Particle number emission factors and their repartition for DPW combustions at 800°C under 50 NL/h of air.

	DS	DPR	DPL	DPT
Total PM_{10} (particles/g biomass)	$10\ 10^{12}$	$45\ 10^{12}$	$16\ 10^{12}$	$54\ 10^{12}$
Total PM_1 (particles/g biomass)	$10\ 10^{12}$	$45\ 10^{12}$	$16\ 10^{12}$	$54\ 10^{12}$
Total $PM_{0.1}$ (particles/g biomass)	$7\ 10^{12}$	$41\ 10^{12}$	$13\ 10^{12}$	$51\ 10^{12}$
$PM_{0.1}$ (%)	72.3	91.2	82.4	94.5
$PM_{0.1–1}$ (%)	27.3	8.8	17.6	5.5
$PM_{1–2.5}$ (%)	0.3	0	0	0
$PM_{2.5–10}$ (%)	0.1	0	0	0

DS and $41\ 10^{12}$, $13\ 10^{12}$ and $51\ 10^{12}$ for DPL, DPR and DPT, respectively. These ultrafine particles, characterized by a small diameter below 0.1 μm, represent a real risk for human health, because they easily penetrate the alveoli of the lungs. Because DS generates the lowest amount of ultrafine particles, this result again underlines the different thermal behavior of this palm waste residue, and its combustion would slightly reduce the negative health impact due to fine and ultrafine particles. This different behavior may be explained by the different ash contents of the initial by-products. Indeed, DS which is characterized by the lowest ash content, generates less fine particles than the other DPW.

Biomass combustion devices need post-treatment systems to remove ultrafine particles from the exhaust. While it was not possible to set up such a system in the laboratory device used in this study, solutions to reduce particulate matter exist, and are already used in residential/industrial biomass heating units (Dickenson, 1997; Ohlstrom *et al.*, 2007; Le Cloirec, 2012; Le Coq, 2012). The two main post-treatment processes for the elimination of ultrafine particles ($PM_{0.1}$) in exhaust are electrostatic precipitation (ESP) and the use of fabric filters. An ESP captures dust

particles by ionizing flue gas in high voltage coronas that charge particles. An electrical field is used to move the particles onto large, flat collecting electrodes which are regenerated by vibration, rapping or scrubbing (Laitinen, 2007; Hartmann *et al.*, 2008; Henriksen, 2008). Fabric filters works by forcing flue gas to pass through a permeable fabric on which dust particles are deposited. These emission factors are very close to those found for energetic crops, such as Miscanthus and Arundo Donax, during previous laboratory scale combustion tests (Jeguirim *et al.*, 2010; Dorge *et al.*, 2011).

The parametric study was completed by carrying out experiments performed at 25 NL/h and 50 NL/h for DS at 800°C. The increase in the air flow rate during combustion of DS from 25 NL/h to 50 NL/h increased the total number of PM_{10} from $5.8\ 10^{12}$ to $10\ 10^{12}$ particles per gram of biomass. This is because a decrease in the gas flow rate increases the residence time of gas in the reactor, and favors the complete oxidation of gas and particles.

Combustion of DS at 500°C was also performed in order to study of the influence of the temperature. Combustion at 500°C takes much more time to carry out, and leads to incomplete combustion with higher amount of tars and

particles (the total number of PM_{10} is 44 10^{12} and 10 10^{12} particles per gram of biomass for combustion of DS at 500°C and 800°C, respectively). If tars are not formed at 800°C, they represent 41% of the total number of particles at 500°C. Figs. 7(a) and 7(b) plot the number size distributions for DS at both temperatures under an air flow rate of 50 NL/h. At 500°C (Fig. 7(a)), the nucleation mode dominates both the flaming phase and the emission of tars, with a number size distribution centered at 0.04 μm. Char combustion generates particles centered at 0.1 μm. At 800°C (Fig. 7(b)), both phases produce particles centered at 0.1 μm. The number size distributions of PM_{10} for DPW at 800°C, including the different phases of the combustion process, are given in Fig. 8. Apart from DS, the combustion of DPL, DPR and DPT leads to the formation of three

phases (solid, liquid and gas). Combustion of DPL, DPR and DPT mainly generates VOC in the form of organic condensable compounds, as tars. As explained above, these tars condense on the top walls of the reactor and are volatilized when the reactor returns to its initial position. The volatilization of these tars corresponds to the main fraction of PM_{10} for DPR and DPT. These tars are composed of ultrafine particles, with a mean geometric diameter centered at 74 nm, and they represent 51% and 54% of the total number of particles for DPR and DPT, respectively. These two palm residues show very similar aerosol fractions in number and size distribution during the three phases of the combustion process. As shown in Table 1, their ultimate and proximate analyses are similar, because the palm rachis is an extension the palm trunk in
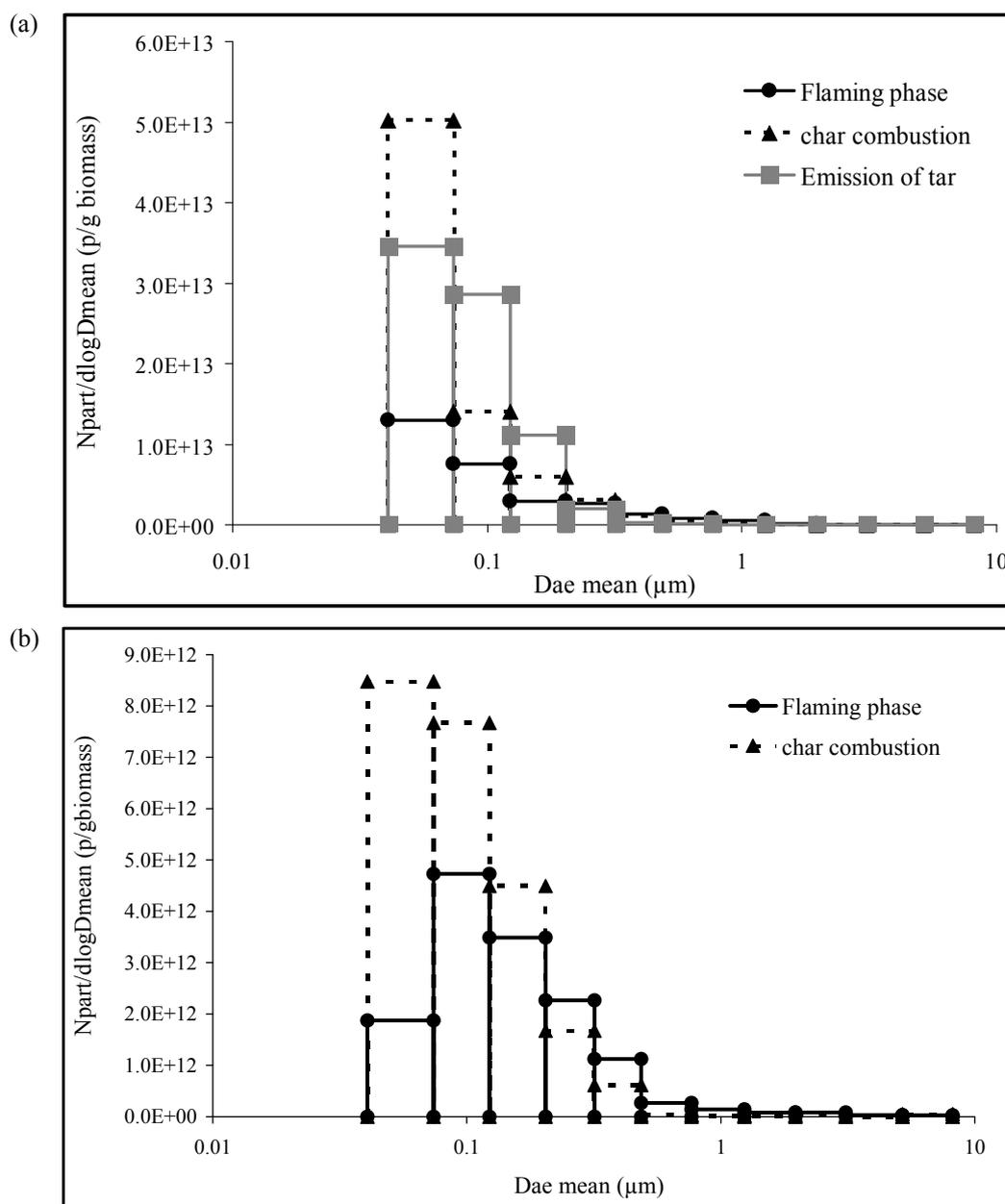

Fig. 7. Number size distributions of PM_{10} for DS at (a) 500°C and (b) 800°C under an air flow rate of 50 NL/h.
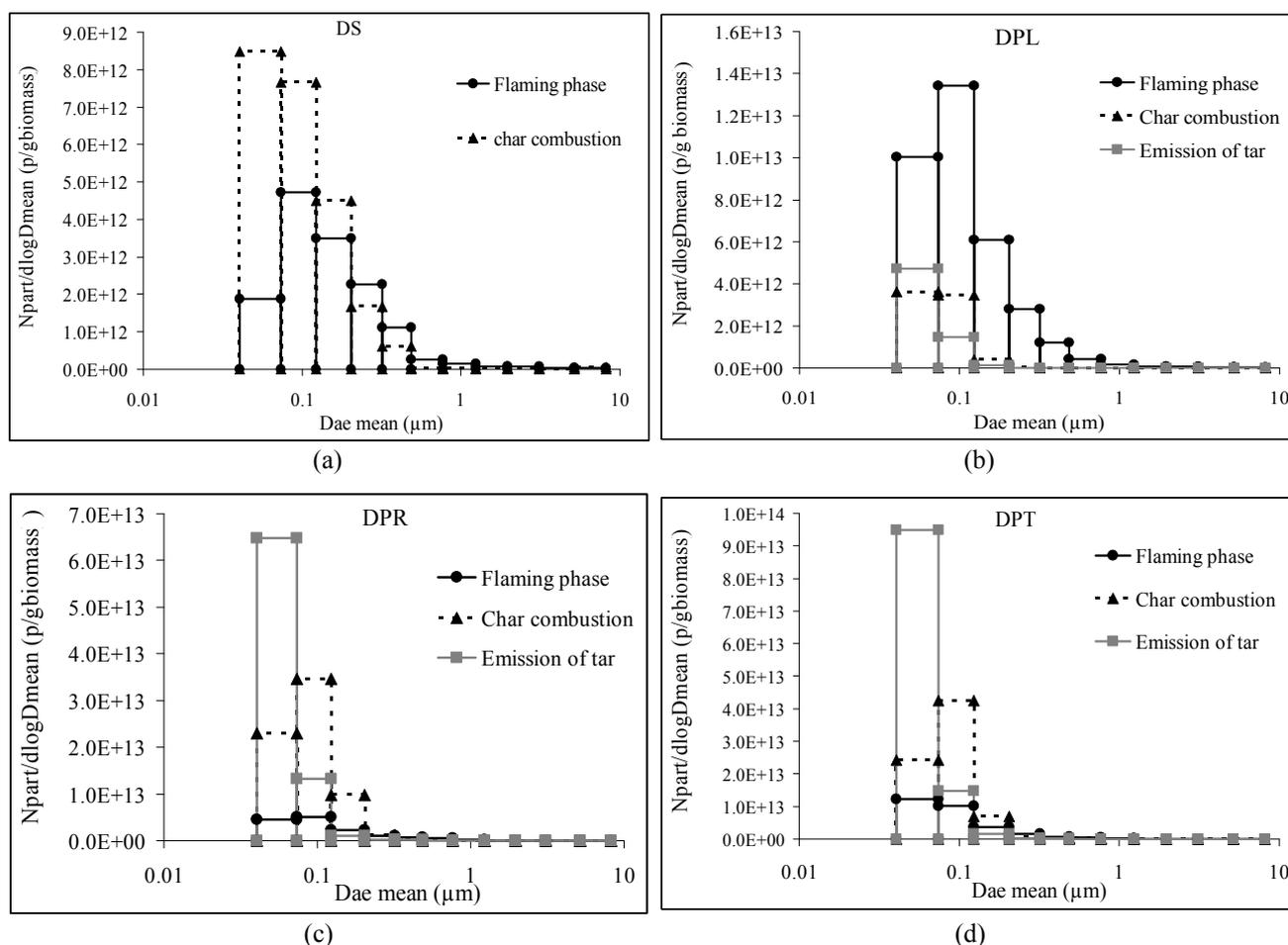
Fig. 8. Number size distributions of PM_{10} for (a) DS, (b) DPL, (c) DPR and (d) DPT during the different steps of the combustion at 800°C under an air flow rate of 50 NL/h.

the palm tree. Although DPL produces a lower tar fraction of aerosols than DPR and DPT, the size distribution is similar, centered at 74 nm. Tars represent 13% of the total number of particles for DPL. Similar to the results shown in Table 1, these DPW contain sufficient amounts of elemental chlorine that is easily volatilized at high temperature, leading to the formation of fine particles, according to Jenkins *et al.* (1998) and Sippula *et al.* (2008). As shown in Table 4, the total number of PM_{10}, PM_1 and $PM_{0.1}$ particles increases with the content of chlorine in the residue. One hypothesis for this is that the amount of chlorine in the residue is related to the formation of tars. Combustion of both DPR and DPT, which have the highest amounts of chlorine, leads to the formation of the highest fraction of tar particles in the exhaust. In contrast, DS, which has the lowest proportion of chlorine, does not form tars during combustion. However, further experiments are needed to analyze the organic fractions of tars in order to identify their chemical compositions. It would be very informative to know whether the elemental chlorine present in DPW is transferred to tars during combustion. Persistent organic pollutants, such as polychlorodibenzodioxins, polychlorodibenzofurans and polychlorobiphenyls, are mainly emitted during combustion of solid residues containing chlorine (Jenkins *et al.*, 1998;

Sippula *et al.*, 2008), these are regulated due to their adverse health effects.

CONCLUSION

Tunisia generates huge amounts of agricultural biomass residues each year that could potentially be used as an alternative fuel source. The proximate and ultimate analyses of four date palm wastes undertaken in this work show their different chemical and physical properties. With the highest bulk densities and the least chlorine and humidity, DPL and DS appear to be the most suitable residues for energy recovery. In contrast, the high amounts of chlorine in DPR and DPT raise the risks of corrosion in the exchange boiler tubes during combustion in district or domestic appliances. Preliminary combustion tests of the four date palm wastes were performed at temperatures between 500°C to 800°C in order to study their thermal behaviors. Fibrous samples, such as DPL, DPR and DPT, ignited very quickly compared to DS at both temperatures. An increase in temperature raised the effectiveness of the thermal process for all samples. Emissions of carbon oxides, volatile organic compounds, tars and particles were observed for all samples at 500°C. In addition, high

molar proportions of carbon monoxide were emitted due to the very short residence time of the gases in the hot zone of the furnace. Among the samples examined in this study, those with low bulk density were affected least by increases in temperature, and their total carbon emission factors all improved, i.e. reduced, with the rise in temperature. However, this was not observed for DS, as its carbon balance sheet did not change significantly when the temperature rose from 500°C to 800°C. Combustion of DPW mainly leads to the emission of ultrafine PM_1, with the nanoparticle $PM_{0.1}$ being the dominant form of this. During the burning process, char combustion was the phase that generated the highest amount of particles at 800°C. At a temperature of 500°C, particles were mainly produced during the char combustion and tar devolatilization phases. The emission factors of the DPW examined in this work were very close to of other energetic crops and conventional biomasses. At 800°C, aerosols from tars were dependent on the initial amount of elemental chlorine in the palm residue, and the number size distribution of the tar fraction was centered at a diameter of 74 nm. The total number of size fractions for PM_{10}, PM_1 and $PM_{0.1}$ was also dependent on the content of chlorine in the residue. With regards to aerosol emissions, optimization of the combustion of date palm by-products may be most efficient at high temperature and low air flow rate. Date stone (DS) has a high energetic density and low content of elemental chlorine, and thus can be burned with low emissions of tars and particles. With regard to the chemical, physical and thermal properties of DPW, this study demonstrated that these materials have some potential for use as energy sources. In order to minimize the related transportation costs and environmental impacts, future experimental work will focus on combustion tests of date stone residues in a pellet boiler working at a power range of 10 to 40 kW, with measurements of normalized pollutants according the EN 303-5 standard. These experiments are already in progress.

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