

THERMOGRAVIMETRIC INVESTIGATION AND THERMAL CONVERSION KINETICS OF TYPICAL NORTH AFRICAN AND MIDDLE EASTERN LIGNOCELLULOSIC WASTES

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The aim of this work was to thermally characterize the renewable lignocellulosic bioresources derived from palm trees in order to highlight their energy potential. Pyrolysis and combustion behaviours of date stones (DS) agricultural by-products were tested by thermo-gravimetric analysis, and the main chemical compositions were analyzed. The work has also been conducted to identify their most important physical characteristics. The study of the sizes and heating rate effects constitute the first part of the experimental work. Inert atmosphere and three heating rates: 10, 20, and 50 °C/min, were applied to various particle sizes of DS. In the second part, tests were carried out in an oxidizing atmosphere (21% O₂) by varying the size of the DS. The kinetic parameters such as pre-exponential factor and activation energy were determined. Increasing the particle sizes and the heating rates didn't have an appreciable influence on the global weight losses. However, degradation rates were significant with the porous structure of the DS. Weight losses in inert and oxidizing atmospheres were found to occur in two stages (drying and devolatilization) and in three stages (drying, devolatilization, and oxidation of the char).

Keywords: Renewable energy; Pyrolysis; Combustion; Thermogravimetric analysis; Lignocellulosic by-products; Kinetics

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INTRODUCTION

The recognised effects of climate change have prompted an urgent appraisal of realistic alternative power generation options. There are various forms of alternative energy sources, such as solar, wind, biogas/biomass, tidal, geothermal, fuel cell, hydrogen energy, etc. The attraction of these sources lies primarily in their abundance and ready access. The Renewable Energy Technologies (RETs) for exploiting these sources include biogas plants, solar lanterns, solar home lighting systems, improved cook stoves, improved kerosene lanterns, solar water pumping systems, solar water heating systems, and water mills. Currently, these options cannot replace the totality of fossil fuel exploitation, but the basic concept of alternative energy relates to issues of sustainability, renewability, and pollution reduction.

In this context, one of these options is to replace a part of fossil fuel with a renewable energy source such as lignocellulosic biomass. Fossil fuels – first coal, then petrol, diesel, and natural gas – have dominated our fuel market. In spite of this, biomass in the form of fuelwood continues to be a major source of energy to this day.

Nearly 70% of India's cooking energy requirement and 32% of its primary energy requirement is met with biomass (MNRE 2009). Globally, fuelwood in its various forms accounts for about 64% of the estimated total world supply of combustible renewable energy sources (Demirbas et al. 2009). The estimates of worldwide annual generation of electricity from biomass amount to about 185 TWh, of which nearly three quarters are produced from solid biomass, 14% from biogas, and 12% from municipal solid waste. If we consider the portion contributed by biomass to the world's total energy production, it comes to only less than 2% (World Energy Council 2007).

For some regions in the world, namely North African and Middle Eastern countries, fossil fuel sources of oil, gas, and coal are predictably running out. Pressures exerted by population and economic growth as well as desalination needs increase demand for electricity (Rogner and Abdel-Hamid 2008). In fact, Tunisia and Morocco are already energy importers, while resources in Algeria, Libya, and Egypt are likely to be exhausted in a couple of generations. These countries must research other sources of energy recovery, with a special emphasis on the usage of agricultural waste.

The date palm tree has been considered an important resource for thousands of years. Dates are used as a raw material in many food industries, as well as a constituent in some animal feeds. In addition to the fruit itself, almost every part of the tree is put to use. Wastes of palm trees, which are produced in huge amounts in North Africa and the Middle East, have proved to be excellent biofuels (Hamada et al. 2002). Haimour and Emeish (2006) found that date stones constitute approximately 10% of the fruit's weight, while Al-Badri and Lafta (1989) found that about 14% of the fruit's weight is waste material. Adapted from a number of literature references according to Food and Agriculture Organization (FAO) to agricultural services, carbohydrates are the major components of date stones (Barreveld 1993). Indeed, these palm trees by-products are composed of cellulose (42%), hemicellulose (18%), lignin (11%), ash (4%), sugar and other compounds (25%).

Energy processes based on lignocellulosic biomass can be divided into two broad categories: biological (fermentation and anaerobic digestion) and thermochemical (combustion, gasification, and pyrolysis). These latter processes can significantly and immediately reduce the mass and volume of wastes, and allow for energy recovery.

In order to evaluate the thermal decomposition of the material, thermoanalytical techniques, in particular thermogravimetry (TGA) and derivative thermogravimetry (DTG), provide basic information in a relatively simple and straightforward manner. Generally, neither a systematic classification of biomass fuels, based on thermogravimetric analysis, nor a general mechanism to interpret such measurements are available, especially for such specific types of lignocellulosic matter.

The aim of the present work was to study the pyrolytic and combustion behaviour of lignocellulosic material (palm by-products) and to obtain a variety of pyrolysis data by changing some factors, namely particle size, heat flow, and reaction atmosphere, with the ultimate purpose of using this kind of biomass for energy recovery and to promote the

possibility of developing an uncomplicated thermal conversion technology system for co-pyrolysis, co-combustion, or co-gasification with wood. Thereafter, it will be interesting to develop new strategies on a larger scale, such as setting up facilities near small farms, making it possible to investigate the practical usage of lignocellulosic bioresources.

For the purpose of this research, date stones from palm trees were investigated: (named hereafter DS). Palm trees produce also another type of lignocellulosic by-product, which is palm stalk (PS). These agricultural wastes originated from Djerid, an area located in the south of Tunisia. A particular attention has been paid to investigate thermal analyses for DS after confirming the close similarity of these two lignocellulosic by-products. After drying at a temperature that didn't exceed 50 °C during 72 hours, these palm by-products were ground to a desirable particle size and sieved to a powder of less than 1mm in diameter and kept in a desiccator to protect them from recapturing the hygroscopic moisture. DS was concerned for TGA/DTG analysis and kinetic parameter determination.

EXPERIMENTAL SETUP AND CHARACTERIZATION

In order to characterize DS and PS in a thermal setting, different analyses were conducted (Table 1).

Proximate Analyses

Moisture was determined by steaming at 105 °C for 24 hours, until a constant mass is achieved. The mineral matter was determined by calcinations at 550°C during 15 min, and the fat matter was quantified by the Soxhlet method.

The higher heating value of ground samples was measured using an adiabatic oxygen bomb calorimeter (Prolabo model) under 25 bars. The energy content of the dry matter was then calculated.

Ultimate Analyses

Carbon, hydrogen, and nitrogen compositions were determined by total combustion at 1050 °C under an oxygen flow. Carbon and hydrogen were transformed respectively into quantified carbon dioxide and water, either by catharometry or by specific infrared detectors. Nitrogen from the samples was transformed into various oxides of nitrogen, which were reduced in molecular nitrogen before being quantified by thermal conductometry. Sulphur content was determined by an analyzer type LECO (model SC 144) performing total combustion at 1350 °C under an oxygen flow. It was transformed into sulphur dioxide, quantified using an infrared-specific detector.

Chlorine was determined by mineralization in an oxygen atmosphere by a combustion type SCHONIGER. Quantitative obtaining of the element in the form of chlorine allows proportioning with silver nitrate by an ordinary potentiometer. Oxygen was determined by the difference. All the experimental tests were carried out in triplicate.

Structural Characterization

The morphology and the chemical distribution of the elements on the surface of raw material were examined using scanning electron microscopy, combined with the

ability to generate localised chemical information through Energy dispersive X-ray spectroscopy (EDX) under ultra-vacuum (Fei Quanta 200).

X-ray patterns were recorded with a Panalytical X'Pert PROMPD diffractometer with a wavelength of 1.789 Å. The X-ray patterns were recorded in the 2θ range 0 to 70° with a scan rate of 0.017° min⁻¹. All the samples were films with similar thickness of 0.3 mm.

Thermogravimetric Analyses

The first part of TGA/DTG experiments was performed using a SETARAM/SETSYS Evolution balance. Approximately 27 to 53 mg of DS samples were placed in the pan of the TGA microbalance, which was operated under a constant purge flow rate of 20 ml/min of Argon under a pressure of 1032 mbar.

Three heating rates were applied (10, 20, and 50 °C/min) for 1.18 mm, 2.36 mm, and 4.75 mm of DS and the powdered form. Residual weight of these samples and the derivative of weight, with respect to time and temperature (differential thermogravimetry analysis, DTG), were recorded using TGA software. Temperature instructions went from 40 to 1000 °C.

The second part of the TGA/DTG experiments was carried out with a thermo standard balance SETSYS 1750 devoted to combustion under 21% of O₂ at 10 °C/min.

RESULTS AND DISCUSSION

Ultimate and Proximate Analyses

The higher heating values of DS and PS were respectively 22.27 MJ.kg⁻¹ and 19.66 MJ.kg⁻¹, which were higher than the energy content of a multiple agricultural by-product such as rapeseed straw (17.64 MJ.kg⁻¹) (Karaosmanoglu et al. 2001), pine chips (18.98 MJ.kg⁻¹) (Sensoz et al. 2002), rice husk (14.42- 18.31 MJ.kg⁻¹) (Mansaray and Ghaly 1997a), and wood (19.10 MJ.kg⁻¹) (Kastanaki and Vamvuka 2006). Moisture related to the rough weight is about 8.00% and 5.8% for DS and PS, compared to 20% for dried wood and 45% for fresh wood. Table 1 summarizes the composition of DS and PS.

Table 1. Proximate and Ultimate Analyses of Palm Trees By-products

Ultimate analyses (wt % dry)	DS sample	PS	Wood (Kastanaki et al. 2006)
C	45.80	44.52	49.60
H	6.28	5.73	6.58
O	46.60	48.08	37.35
N	0.81	0.17	4.19
S	0.22	0.00	0.12
Cl	<0.20	nd	nd
Proximate analysis (wt% dry)			
Ash	1.12	1.50	2.16
Fat	8.00	2.00	-
Volatile matters	45.08	48.18	76.33

Scanning Electron Microscopy/ EDX Ultra-Vacuum

Scanning electron micrographs of raw DS and PS are shown in Fig. 1. The examination of the initial structure of the DS shows the presence of a few macropores (Fig. 1a) of various size and geometry on the surface. However, it is a fibrous form of PS (Fig. 1b).

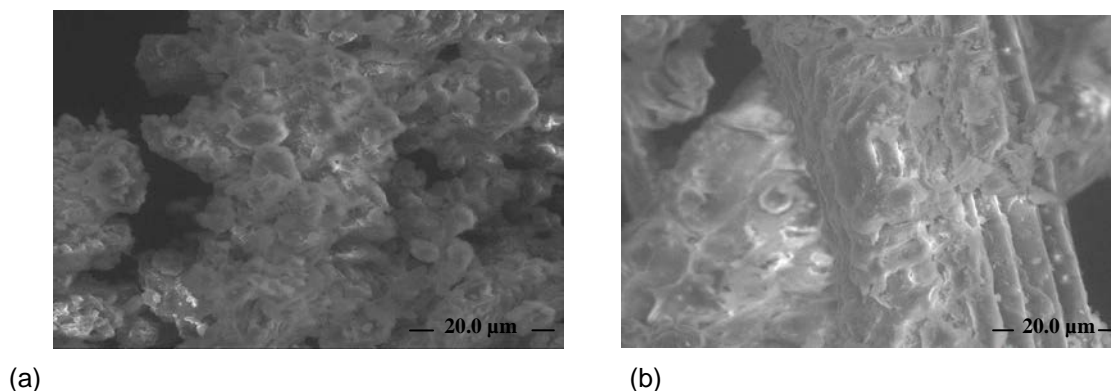


Fig. 1. Scanning electron micrographs of (a) DS and (b) PS samples

More than one zone of the surface was analysed, since the chemical elements distribution is heterogeneous (Table 1).

These surfaces were the first contact field for many thermal transfer interactions during the thermal conversion process of the matter. With regard to the mineral content (Tables 2 and 3), it was found that the external surfaces of DS show appreciable amounts of carbon, and oxygen. Among the elements present in a few amounts in the DS matter are cobalt, aluminium, silicon, etc. Iron, chlorine, phosphorus, magnesium and others element were considered as traces.

Table 2. EDAX Quantification of DS and PS surface (Powder)

Elements (wt%)	DS		PS		
	Zone 1	Zone 2	Zone 1	Zone 2	Zone 3
C	64.53	62.26	66.80	62.52	71.34
O	33.63	35.85	31.14	30.37	27.48
Co	0.93	0.97	0.82	-	0.84
Mg	0.08	0.09	0.12	0.16	0.10
Al	0.17	0.17	0.19	0.11	0.06
Si	0.28	0.27	-	0.09	0.03
P	0.04	0.04	-	-	-
S	0.03	0.04	0.06	0.18	0.02
Cl	0.03	0.04	0.34	2.65	0.04
K	0.14	0.15	0.47	3.92	0.09
Ca	0.07	0.08	-	-	-
Fe	0.06	0.05	-	-	-
Na	-	-	0.06	-	-

Table 3. EDAX Quantification of DS and PS surface (Particle)

Elements (wt%)	DS		PS
	External Surface	Internal Surface	External Surface
C	58.38	59.13	82.59
O	37.31	37.91	13.48
Co	1.13	1.04	-
Mg	0.13	0.13	0.23
Al	0.30	0.30	0.37
Si	0.64	0.54	0.85
P	0.12	0.08	0.03
S	0.07	0.07	0.26
Cl	0.33	0.12	0.30
K	0.76	0.34	0.34
Ca	0.62	0.18	0.66
Fe	0.18	0.15	0.21
Na	-	-	0.17

Similar to the DS sample, external surfaces of PS show appreciable quantities of carbon, and oxygen, rather a significant amounts of chlorine and potassium. Silicon, calcium, phosphorus and potassium are known to be plant nutrients and soil improvement agents (Steenari and Lindqvist 1997). The distribution of chemical elements shows that the raw materials are highly heterogeneous depending on the form of the ground DS and PS. The potassium ion is one of the most abundant ions that naturally occur in native material.

It is important to identify the inorganic element distributions since they have an important effect on the pyrolysis temperature and on the products' composition (char, tar, and gases).

On the other hand, when some research opts for a large scale application to investigate this lignocellulosic matter, it is necessary to highlight that high amounts of inorganic constituents in some lignocellulosic biomasses contribute to adverse impact on the different elements of the conversion systems. The chlorine and potassium in biomass are water-soluble, they can largely be removed through leaching, thus mitigating their impact on high temperature conversion devices. Water washing is a means to eliminate some metals, thus improving behaviour during thermal treatments (Jenkins et al. 1996).

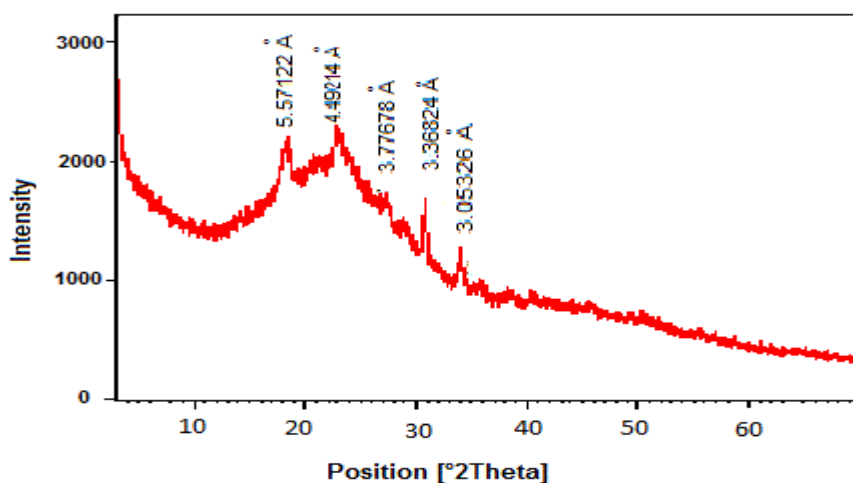
Table 4. Elemental Compositions of the Raw Materials

Elements mg/g	DS	PS
Cu	0.06	0.06
Mg	1.26	2.43
Fe	1.2	0.2
K	6.36	27.06
Ca	1.73	7.27
Mn	0	0
Cd	0	0
Zn	0	0.56
Al	0.4	0.06

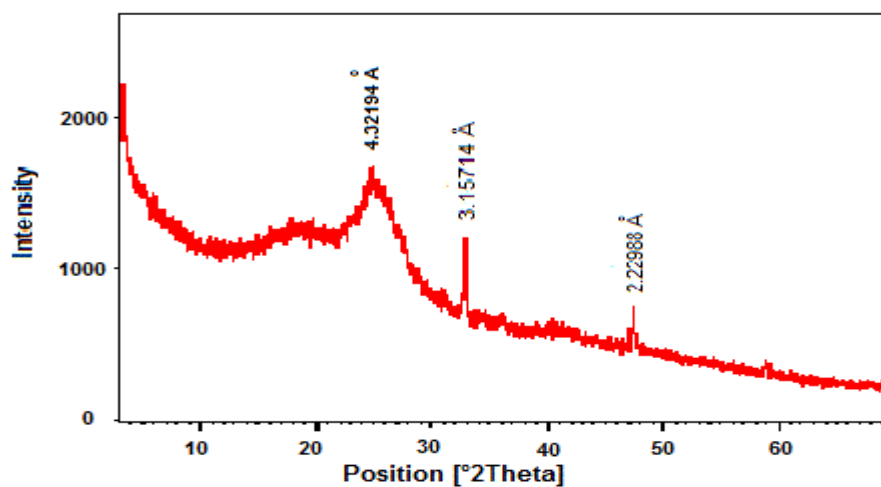
Ash constituents, especially potassium, sodium, and calcium, act as catalysts for the decomposition process and favour char formation (Jensen et al. 1998 ; Fahmi et al. 2007). Chemical analyses of inorganic elements in the raw materials are given in Table 4. It can be noticed that this type of by-product shows an absence of heavy metals.

XRD Analysis

X-ray diffraction patterns of natural DS and PS are given in Fig. 2. The diffractogram of natural DS does not exhibit a horizontal basic line. This shows that the major part of the matter is amorphous. However, a few diffraction peaks emerge from the basic line, indicating the presence of a small amount of crystalline matter.



(a)



(b)

Fig. 2. XRD patterns of (a) (DS) and (b) (PS)

The XRD pattern of natural date pits has been compared to those of native cellulose ($C_6 H_{12} O_6$), xylane dehydrate ($C_{10} H_{12} O_{9.2} H_2 O$), or hemicellulose dehydrate given in the JCPDF crystallographic data base (Table 5) (Zhao et al. 2007).

Table 5. Bragg Diffraction Angle ($^{\circ}2\theta$) and Reticular Distance (d) of DS and their Corresponding Compounds Identified in the JCPDF Crystallographic Data Base (N.CI : native cellulose, HCel : hemicellulose dehydrate, C : carbon)

Pos. [$^{\circ}2\theta$.]	d(Å)	Corresponding compounds
18.4921	5.57122	N.Cel and HCel
22.9887	4.49214	N.Cel and HCel
27.4209	3.77678	C
30.8246	3.36824	HCel
38.5353	2.71274	N.Cel and HCel

Characterization studies on biomass samples are quite important to judge suitability of feedstock for thermochemical conversion. The two lignocellulosic materials presented and characterized above showed a very close similarity. However, because of the important higher heating value of DS sample, we have chosen DS to investigate thermal gravimetric analyses and to show more detail for the thermal degradation behaviors.

Inert Atmosphere

TGA analyses were operated under a constant purge flow rate of 20 mL/min of Argon. Three heating rates were applied at 10, 20, and 50 $^{\circ}C/min$.

Typical representations of TGA/DTG diagram for DS are shown in Fig. 3 under inert atmosphere and with a heating rate of 10 $^{\circ}C/min$. The raw DS diagram shows three stages; drying, fast pyrolysis, and slow pyrolysis.

The first stage of weight loss ranged from 47 $^{\circ}C$ to around 160 $^{\circ}C$ (Fig. 3). The derivative plot (DTG) had a separate peak for this step of thermal process, which was attributed to the moisture loss and probably some volatile compounds in the biomass sample so that the low moisture content resulted in low weight loss during this stage.

The second stage corresponding to fast pyrolysis had three zones. Following this stage, the first zone (Z 1) showed a negligible weight loss ($\approx 5\%$) in the temperature range of 135 $^{\circ}C$ to 230 $^{\circ}C$, this phase was identified as the beginning of the decomposition of cellulose and hemicellulose. The second zone (Z 2) started around 230 $^{\circ}C$ and extended to 330 $^{\circ}C$. Weight loss during this stage was rapid; it was the active pyrolysis step so the second stage was designated as the fast pyrolysis.

Zone 3 of the fast pyrolysis stage showed a rapid weight loss, but relatively less important (20%) than the previous stage, which probably corresponds to the first step of lignin decomposition; this indicates that the amount of lignin is significant in the raw DS.

It was concluded that the most distinguished peak in fast pyrolysis stage is related to the complete pyrolysis of hemicellulose, which took place until 350 $^{\circ}C$, while the pyrolysis of cellulose occurred from 250 $^{\circ}C$ to 500 $^{\circ}C$ (Fig. 3). The same results have

been reported in the literature concerning thermal degradation of rice husks (Manasary and Ghaly 1998c; Varhegyi et al. 1997).

Kilzer and Broido (1965) have proposed a general kinetic scheme for the pyrolysis of pure cellulose. Its decomposition would occur according to two competitive reactions occurring directly from cellulose. The first one (473 to 553 °C) is a slightly endothermic reaction of dehydration, followed by an exothermal process that produces char and light gaseous species. In the second one (553 to 613 °C), cellulose is postulated to be transformed into an intermediate and unstable compound. A similar scheme has been proposed by Arsenau (1971).

The derivative plot of the region between 230 °C and 500 °C showed two observable peaks but a slow degradation of biomass continued until 900 °C, at which point complete devolatilization occurred.

It can be seen that the lignin degradation was slow and occurred over a wide range of temperatures (Vamvuka et al. 2003a). Following this stage, there was a continuous and slow weight loss from 500 °C to 1000 °C; this stage was so-called “slow pyrolysis,” and could be a thermal continuity of decomposition of lignin and other compounds with high molecular weights.

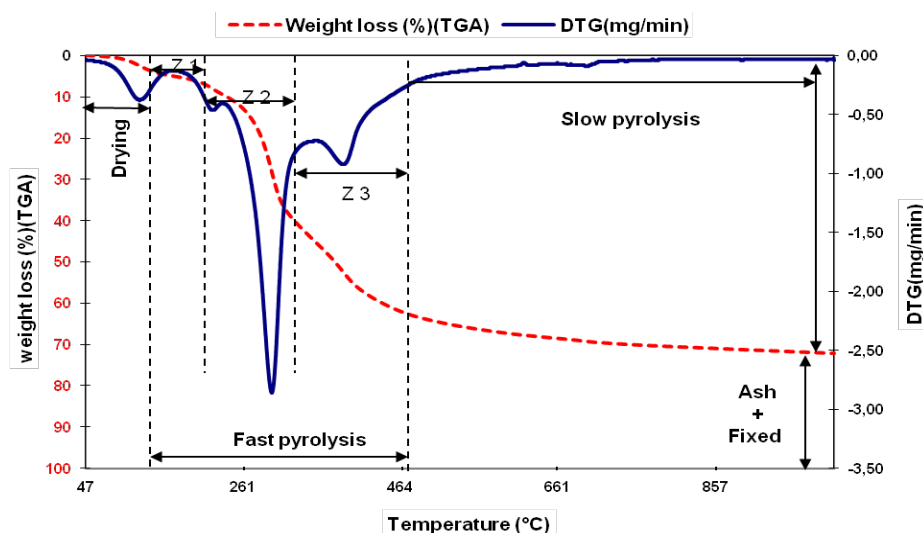


Fig. 3. Typical TGA diagram of DS (powder) in an Argon atmosphere (10 °C/min)

Such thermal behaviour can be explained by the structural differences in lignin, cellulose, and hemicellulose. Cellulose and hemicellulose are basically composed of polysaccharides. On the other hand, lignins are complex racemic polymers derived mainly from three hydroxycinnamyl alcohol monomers that differ in their degree of methoxylation and are heavily cross-linked. Lignin polymerization is characterized by some typical inter-unit linkages.

Thus, lignin has a high thermal stability and it is difficult to decompose (Yang et al. 2006). Lignin pyrolysis takes place at a pyrolysis temperature range from 150 °C to 900 °C, and no sharp weight loss peak appears (Li et al. 2004). Since the cellulosic

compounds have the structure of branching a chain of polysaccharides and no aromatic compounds, that's why their volatilization is easy (Gani and Naruse 2007).

Park, Atreya, and Baum (2010) reported that wood consists of three major components: hemicellulose (25-35%), cellulose (40-50%), and lignin (16-33%), a composition range similar to DS. Each component displays different characteristics during its thermal decomposition. Hemicellulose decomposition occurs at 200-260 °C and produces acetic acid. Cellulose decomposes to levoglucosan and dehydrocellulose at 240-350 °C. Lignin decomposes over a broad temperature range of 280-500 °C and produces more char than the other two components. These temperature ranges for degradation also describe the thermal behaviour of DS, so it is interesting to plan for co-pyrolysis of wood and DS at a large scale.

Effect of heating rate during pyrolysis of date stones

Figures 4 and 5 illustrate the influence of the heating rate on the degradation process of DS (<100 µm and initial weight < 40 mg). Few workers have discussed testing the effect of heating rate on the devolatilization behaviour of biomass. The most common ramp rate reported in the literature for TGA characterisation of biomass appears to be 10 °C/min (Vamvuka et al. 2003b), 20-30 °C/min (Peralta et al. 2002), 50 °C/min (Moghtaderi et al. 2004), or 100 °C/min (Pan et al. 1996), with relatively few using lower heating rates. It is therefore useful to investigate different heating rate profiles. Heating rate had an effect on the temperature range of the stages of the reaction (Fig. 4). Increasing the heating rate appeared to increase the range of temperatures of each stage, which may have been due to the heat transfer limitations.

Three temperatures were recorded: T_{ini} is the temperature where weight loss first reached 0.5 mg/min; T_{peak} is where the weight loss reached its maximum; and T_{end} is where the weight loss fell below 0.5 mg/min. The limit of 0.5 mg/min was established using actual profiles as an arbitrary limit for the start and end for peaks (Fig. 4).

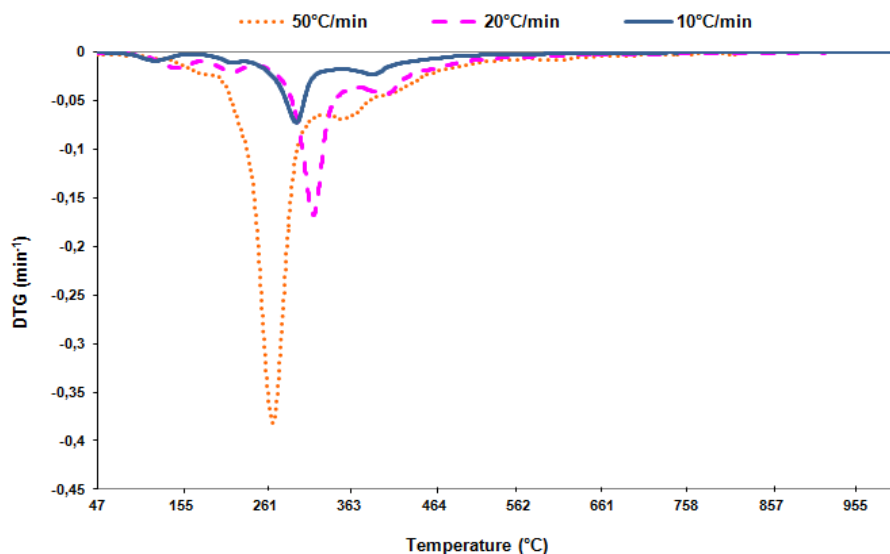


Fig. 4. Effect of heating rate on DTG during pyrolysis of DS

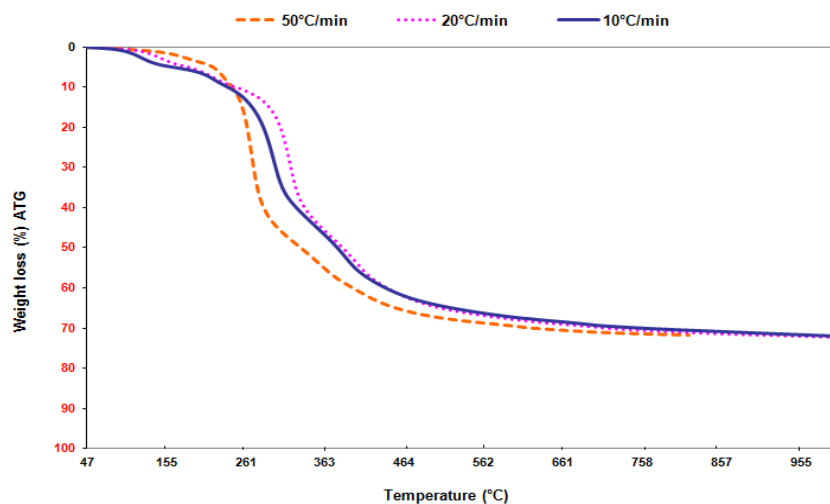


Fig. 5. Effect of heating rate on TGA during pyrolysis of DS

It was expected that the peak temperature would increase with an increasing heating rate. However, in this study, for 50 °C/min there was a lower peak temperature than that registered for 10 °C/min. In fact, high heating rates and large mass loading tend to deflect the measured temperature from the actual sample temperature. It is clear that by increasing the heating rate, a longer time may be required for the purging gas to reach equilibrium with the temperature of the furnace or the sample because of the heat transfer limitations.

Char characterization

Characterization studies on biomass samples are quite important to express suitability of feedstock for thermochemical conversion. High volatile matter content of biomass with low ash and sulphur content is the main criterion for pyrolysis conversion. From the main characteristics of the raw material (Table 1), it appears that the high volatile content of lignocellulosic biomass favours pyrolysis conversion.

Scanning electron microscopy (SEM) was used to characterize the size and the shape of the char particles, as well as their porous surface structure (Fig. 6). Pyrolysis temperature and heating rate influenced the size and shape of particle due to a general increase in size and proportion of voids and a decrease in cell wall thickness. For DS biomass it seemed to be more favourable to apply pyrolysis at 500 °C, where the most highly porous and spherical particles were observed. Fast pyrolysis of DS does not favour the thermal conversion of the matter. At low pyrolysis temperature (Fig. 6b) and low heating rate, no porous structure was seen; the particles were thick-walled and covered by tar agglomerates. The wood sample presented a slightly porous surface at 600 °C and at a slow heating rate; wood samples maintain a rigid aspect, which is due to a natural lignin-developed structure. The diffractogram of DS having undergone pyrolysis under inert gas (Fig. 7) showed significant effects of pyrolysis: several peaks disappeared due to the decomposition of cellulose and hemicellulose during thermal conversion.

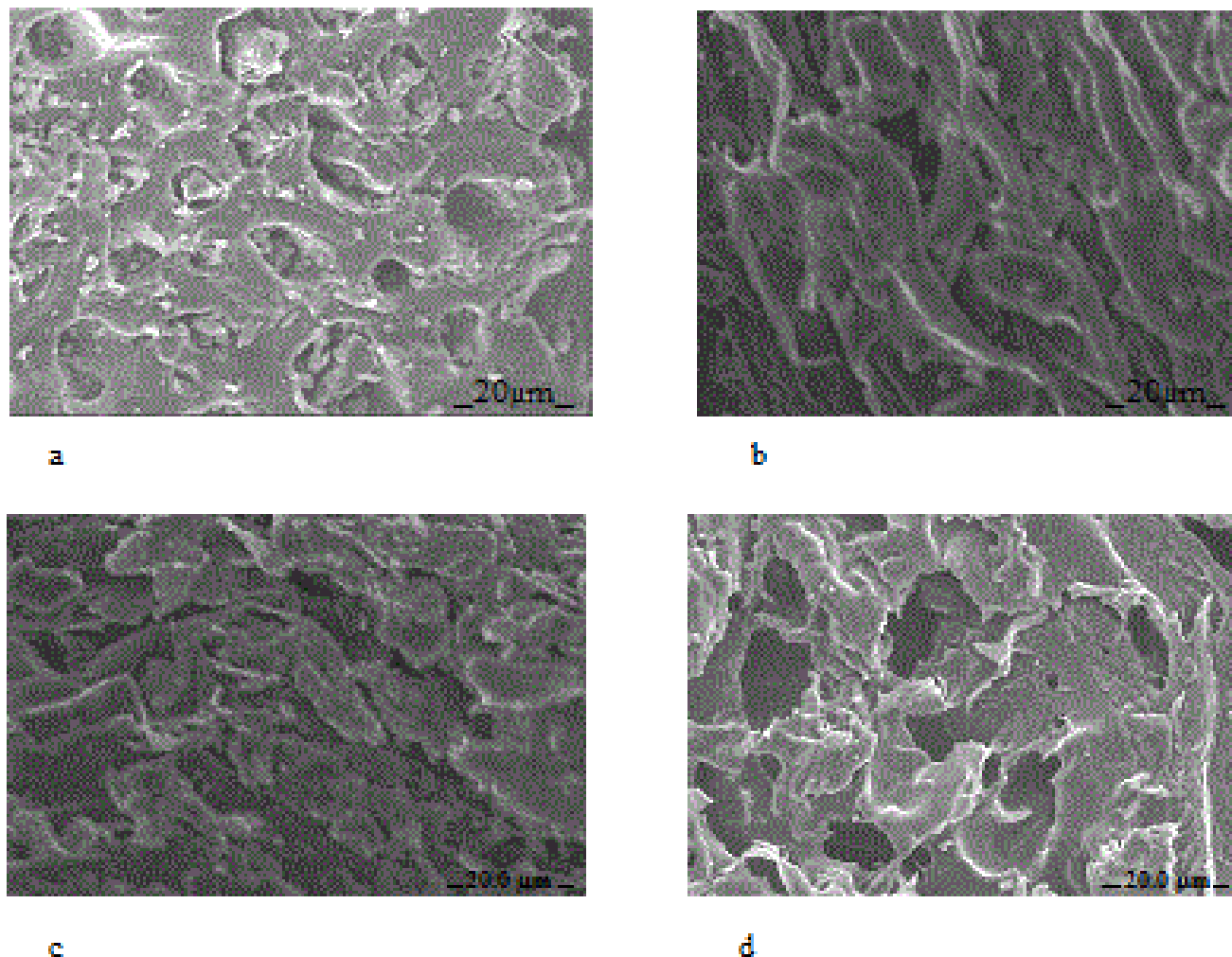


Fig. 6. SEM photomicrographs of char obtained at (a) 500 °C (50 °C/min), (b) 400 °C (10 °C/min), (c) 600 °C (100 °C/min) for DS and (d) 600 °C (10 °C/min) for wood

After pyrolysis, the small amount of crystalline matter was destroyed and no peak of diffraction remained on the baseline of the diffractogram. The nanometric composition of pyrolysed matter was dominated by the presence of carbon. Similarly to wood, DS is mainly composed of the cellulose ($\approx 50\%$). A study has been made on the kinetics of the thermal decomposition of the crystalline cellulose in wood by in situ X ray diffraction (Zickler et al. 2007); in this case the fiber diffraction patterns were studied as a function of heat treatment under temperature ranging from 573 to 633K.

The results show a thermally activated reduction in the microfibril diameters with random breaking of the fibers into shorter species due to anisotropic nature of the material. In our case, we have applied a pyrolysis temperature which increases from the ambient temperature to 1000 °C. The material became amorphous and no peak was discerned.

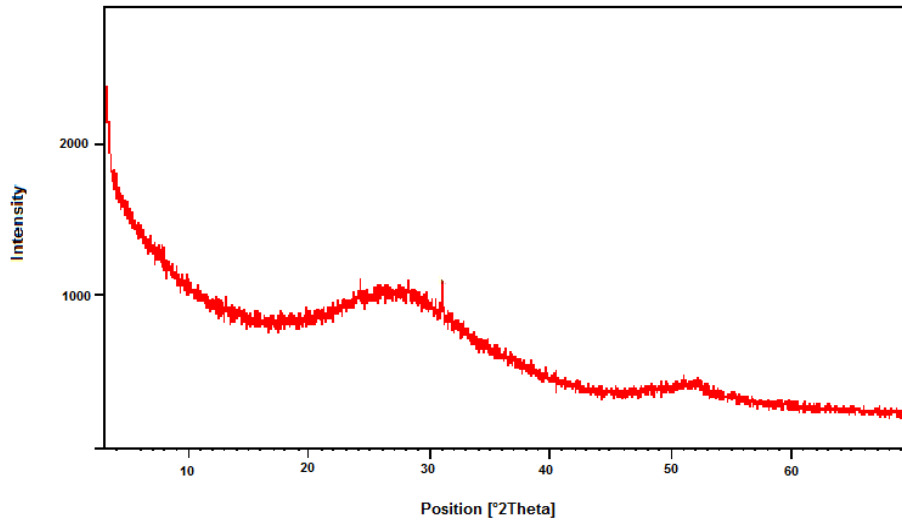


Fig. 7. Diffractogram of pyrolysed DS

Effect of particle sizes during pyrolysis of date stones

Figures 8 and 9 show, respectively, mass loss rates and weight loss for different DS sizes with a fixed heating rate of 10 °C/min. The effects of biomass particle size on its pyrolysis behavior can be directly assessed only for the particles prepared using similar milling and sieving methods for similar types of biomass. Broadly, samples show the same curves for different particle sizes. Particle sizes slightly influence temperature ranges, but more so influence the mass loss rate (Fig. 8).

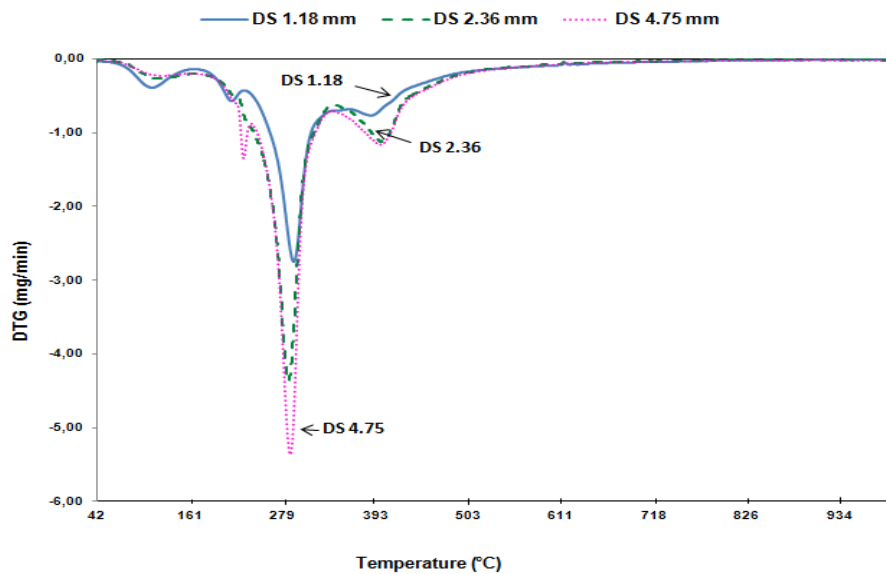


Fig. 8. Mass loss rate of the different particles size of DS

During active pyrolysis as shown in a typical diagram (Stage 2 (Z :1), Fig. 3) and on the same range of temperature for all particle sizes, curves of mass losses show that mass loss rates increased with increasing particle sizes. In this stage, the major compound degrading is hemicellulose, particularly cellulose. Figure 9 shows that the mass losses during active pyrolysis of different particles size varied slightly; however, the variation was more significant when comparing DS powder with DS of 4.75 mm. This presents a difference of around 7% of mass loss. In fact, the degradation rate was favored by the macroporous structure of DS, which remains increasingly intact when the shape and the size of the particles approaches the rough state. As for the lignin decomposition, starting from 500 °C to the end of decomposition, mass loss increased with increasing particles size (Fig. 9), and no effect over the total duration of the decomposition process was observed. The decomposition of lignin was complete around 900 °C.

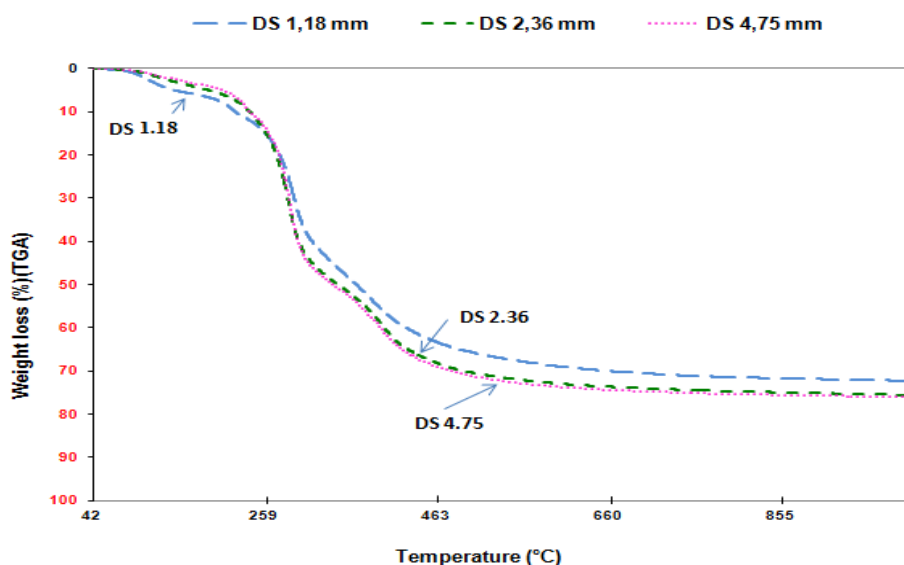


Fig. 9. Effect of particle sizes on TGA during pyrolysis of DS

Air Atmosphere

Figures 10 and 11 show weight loss and loss rate for three various particles size of DS under an oxidizing atmosphere with 10 °C/min of air. TGA plots suggested that there were three stages of weight loss. For 1.18 mm particles of DS, the first stage of weight loss from 48 to 175-180 °C was similar to the first stage in the inert atmosphere. The loss of water and the volatilization of light molecules may have contributed to weight loss in this stage. After that, in the second and third stage, there was minimal variation in the characteristic profiles for each size fraction. For 4.75 mm particles of DS, there were no significant differences compared to the other sizes. Indeed, the mass loss rate reached a maximum of about 0.1 min⁻¹ at 295 °C vs. 0.06 min⁻¹ and 0.09 min⁻¹, respectively, for 1.18 mm and 2.36 mm DS particles for the same temperatures. From Fig. 10 it is clear that our TGA experiments were mass transfer limited; however, DTG experiments (Fig. 11) did not show any real influence of increasing particle size in the conditions of 10 °C/min of air and an important initial weight of raw material, so we have to identify the optimum heating rates.

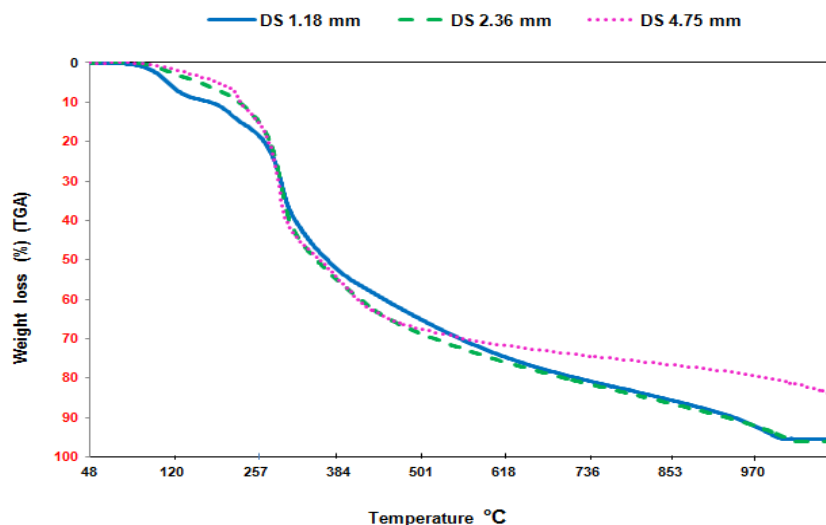


Fig. 10. Effect of particle size on TGA during combustion of DS

Hence, the effects as a result of particle size may have been negated by the choice of a very slow heating rate, allowing the particles to swell and devolatilize being controlled only by furnace temperature.

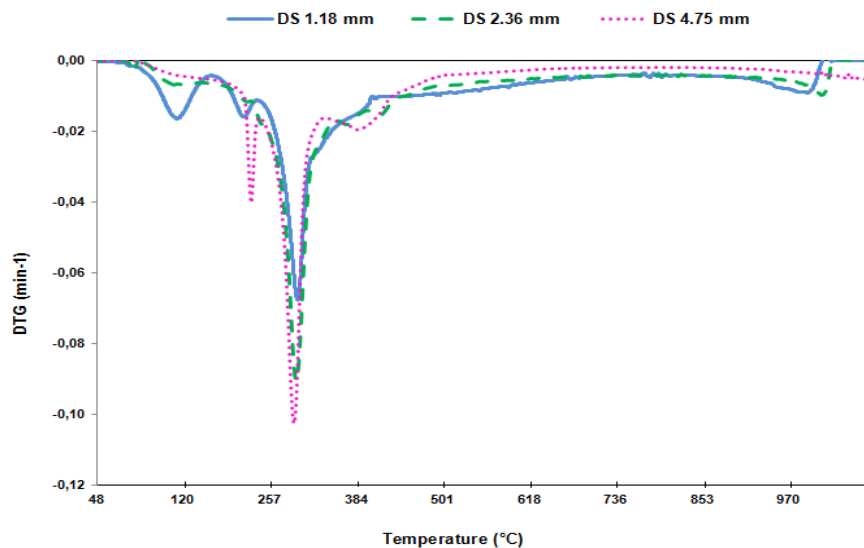


Fig. 11. Effect of particle size on DTG during combustion of DS

Moreover, for 2.36 mm and 4.75 mm particles, it is clear that following water vaporization in the first phase, two other stages of thermal degradation are significant. The first stage can be identified with the degradation of hemicellulose, and the second with cellulose. The decomposition of lignin proceeds in the last stage (slow degradation) (Fig. 10). The second phase of weight loss ranged from 240 °C to 400 °C, which was

more rapid than the other phases. In this region, there was a very important mass loss for all particle sizes, corresponding to the removal of volatile matter. Similar observations have been made, confirming the low reactivity of lignin solid matrix when the temperature of degradation is below 350 °C to 400 °C (Sharma et al. 2004).

It can be concluded that at a slow heating rate of 10 °C/min in an air atmosphere, the weight loss in the first stage was less than 5%, which is similar to that obtained in the inert atmosphere conditions. However, in the second stage of thermal degradation, there was a very large weight loss (> 85%) as compared with the value registered in the inert atmosphere (\approx 65%), which is the result of char oxidation.

Kinetic Study

Chemical kinetics of biomass pyrolysis and combustion degradation coupled with the description of transport phenomena provide advanced computational tools for the design and optimization of chemical reactors used for thermochemical conversion of wood and biomass. The knowledge of the fuel reactivity is also needed for the formulation of simple design and scaling rules.

Thermo-chemical conversion of biomass results from a strong interaction between chemical and physical processes at the levels of both the single particle and the reaction environment. This why kinetic studies of this lignocellulosic material are needed as a tool for the prediction of reactor performance. The literature does not provide any information relating to the kinetic parameters of DS wastes. Nevertheless, a comparison with the values generally recorded for other biomasses give a rough estimate. Several models are applied in the literature.

The kinetic parameters of DS degradation reactions during pyrolysis are based on the Arrhenius equation, which is also used by many researchers (Karasosmanoglu et al. 2001). This model doesn't fix the reaction order (n); rather, this parameter is determined by linear regression.

The overall kinetic reaction is written as follows,

$$\frac{dx}{dt} = kf(x) \quad (1)$$

where x is the weight conversion ratio defined as,

$$x = \left(\frac{w - w_f}{w_0 - w_f} \right) \quad (2)$$

During decomposition, w_0 is the initial biomass sample decomposed to sample mass w at time t , where k is the rate constant and $f(x) = (1-x)n$ and n is the order of reaction. According to the Arrhenius correlation the rate constant k is defined as:

$$k = Ae^{\frac{-E}{RT}} \quad (3)$$

In Eq. 3, A (s^{-1}) is the frequency factor, E (KJ/mol) is the activation energy, T (K) is the reaction temperature, and R (J/K/mol) is the gas constant. Thus we can write the following equation:

$$\ln\left[\frac{-1}{w_0 - w_f} \frac{dw}{dt}\right] = \ln(A) - \left(\frac{E}{RT}\right) + n \ln\left(\frac{w - w_f}{w_0 - w_f}\right) \quad (4)$$

The linear form of this equation is,

$$y = B + Cx + Dz \quad (5)$$

where

$$y = \ln\left[\frac{-1}{w_0 - w_f} \frac{dw}{dt}\right], \quad x = \frac{1}{T}$$

$$z = \ln\left(\frac{w - w_f}{w_0 - w_f}\right)$$

$$B = \ln(A)$$

$$C = \left(-\frac{E}{R}\right)$$

$$D = n$$

The constants B, C, and D were estimated by multi-linear regression of the TGA for each stage using Microsoft Excel. Through previous analysis of thermal degradation behaviour, the weight loss is more important during fast pyrolysis (active degradation), which is why kinetic parameters of this phase must be specified. Beyond the fast pyrolysis, lignin decomposition continues until over a broad temperature range of 700 to 900 °C. It is a slow degradation, characterized by an order 0 of the reaction, indicating a low rate of weight loss.

A difficulty in kinetic analysis also exists in separating the effects of chemistry and transport phenomena. One of the key points in relation to intrusion of heat and mass transfer processes in kinetic analysis is the effect of sample sizes/masses during pyrolysis, which cause spatial gradients of temperature (a process taking place under non-negligible effects of internal heat transfer) or significant differences of temperature between the controlling thermocouple and the sample, especially when these are not in close contact.

Morphology as well as the chemical structure of lignocellulosic sample are the indicative intrinsic parameters of the nature of thermal behaviour during degradation. Indeed the porous structure of DS and the significant quantity of cellulose (42%) enhance thermal degradation.

Table 6 illustrates the variation of the kinetic parameters of the DS sample during pyrolysis in an inert atmosphere in Argon with 10 °C/min for various particle sizes and heating rates. Kinetic parameters of DS degradation reactions for different particles size showed an order of 2.5 and activation energy of about 58 KJ/mol with a value of $R^2 \geq 0.8$

in all cases. On one hand, these results constitute a good approximation. On the other hand, it is clear that in pyrolysis degradation particles size has no important influence on the kinetic parameters.

Table 6. Kinetic Parameters during Active Pyrolysis

	Active pyrolysis (°C)	A (s ⁻¹)	E (kJ/mol)	n	r ²
Heating rate (°C/min)					
10	165-500	720.53	58.4	2.83	0.9
20	170-490	219.20	52.4	2.28	0.8
50	150-500	88.23	44.0	2.22	0.9
Particle sizes (mm) at 10°C/min					
1.18	170-560	830	58.3	2.78	0.9
2.36	170-470	586	57.5	2.43	0.8
4.75	170-480	1040	59.8	2.52	0.8

It should also be noted that, for the conditions of the thermal analysis, the process of lignin and cellulose decomposition are considered to be globally exothermic and endothermic, respectively (Bilbao et al. 1993). During this primary decomposition, secondary reactions effect was kept at a minimum by maintaining the reaction temperature above 800 °C (Di Blasi et al. 2001).

In this global thermal process the data were examined by taking into account the temperature range investigation, which has an upper limit of 900 to 1000 °C. The limited range of temperature of 500 to 560 °C was needed to determine activation energy. This range of thermal process describes the fast pyrolysis phase (Fig. 3). In this case, heating rate had a significant effect on the activation energy variation.

From Table 6 it can be observed that a higher heating rate decreased the activation energy. As it was explained through the pyrolysis thermal degradation process, heating rate influenced the temperature ranges of the pyrolysis process. Also, the thermal degradation rates increased with the heating rate (Fig. 4), which means that global kinetic evolution was favored in this thermal conversion conditions. Combined effects of changes in decomposition temperature ranges at the different heating rates and the kinetics of the devolatilization were observed.

Contrary to the results shown for pyrolysis kinetic degradation (Table 6), for which activation energy was not influenced by particle size, combustion degradation behaviour (Table 7) showed an increasing value of activation energy with increasing particle size.

It seems that the thermal degradation of the DS under oxidizing conditions was influenced by thermal and mass transfer limits.

Table 7. Kinetic Parameters during Active Combustion/Particle Size Effect

	Active combustion (°C)	A (s ⁻¹)	E (kJ/mol)	n	r ²
Particle sizes (mm) at 10 °C/min					
1.18	170-480	1130	58.7	5.60	0.8
2.36	170-480	2360	62.3	5.19	0.8
4.75	170-480	2110	71.7	4.52	0.8

CONCLUSIONS

1. The large amount of available palm trees makes palm biomass resources ideal candidates as future feed stock for bioenergy production with a low cost of pre-treatment experiments.
2. This study addresses for the first time (on a scientific and technical basis) the feasibility of using palm tree by-products, i.e. date stones and palm stalk, as new renewable sources of energy. Indeed, it is important to identify the main physicochemical characterization, and the thermal behavior of these palm trees by-products, in order to extrapolate their energy conversion by combustion and pyrolysis.
3. Properties of these biomasses are interesting from a thermal point of view. However, heating values are even greater than the HHV of wood and for other biomasses quoted in the literature.
4. All of the physico-chemical and thermogravimetric analyses affirm that the thermal valorization of these kinds of palm by-products constitutes a significant alternative to implement a potential new renewable energy source.
5. The physico-chemical and morphological study of these wastes shows that they are characterized by a relatively low moisture content, a high HHV, and an absence of heavy metals, compared to other biomasses.
6. Through thermogravimetric analyses, for both samples and other biomasses, weight losses in inert and oxidizing atmospheres were found to occur respectively in two and three stages (drying – devolatilization and oxidation of the char in combustion tests).
7. The major components of DS (hemicelluloses, cellulose, and lignin) influence the mass loss rate during thermal degradation.

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REFERENCES CITED

- Al-Badri, H. T., Lafta, S., Barbooti, M., and Al-Sammerrai, D. (1989). "The thermogravimetry and pyrolysis of date stones," *Thermochimica Acta* 147(2), 283-289.
- Arseneau, D. F. (1971). "Competitive reaction in the thermal decomposition of cellulose," *Canadian Journal of Chemistry* 49, 632-638.
- Barreveld, W. H. (1993). "Date palm products," *FAO Agricultural Services*, Bulletin no. 101, Food and Agriculture Organization of the United Nations, Rome, Italy.

- Bilbao, R., Millera, A., and Murillo, M. B. (1993). "Temperature profiles and weight loss in the thermal decomposition of large spherical wood particles," *Journal of Industrial and Engineering Chemistry* 32, 1811-1817.
- Bridgeman, T. G., Darvell, L. I., Jones, J. M., Williams, P. T., Fahmi, R., Bridgwater A. V., Barraclough, T., Shield, I., Yates, N., Thain, S. C., and Donnison, I. S. (2007). "Influence of particle size on the analytical and chemical properties of two energy crops," *Fuel* 86(1-2), 60-72.
- Demirbas, M. F., Balat, M., and Balat, H. (2009). "Potential contribution of biomass to the sustainable energy development," *Energy Conversion and Management* 50(7), 1746-1760.
- Di Blasi, C., Branca, C., Santoro, A., and Gonzalez Hernandez, E. (2001). "Pyrolytic behavior and products of some wood varieties," *Combustion and Flame* 124(1-2), 165-177.
- Fahmi, R., Bridgwater, A. V., Darvell, L. I., Jones, J. M., Yates, N., Thain, S., and Donnison, I. S. (2007). "The effect of alkali metals on combustion and pyrolysis of *Lolium* and *Festuca* grasses, switchgrass and wilow," *Fuel* 86(10-11), 1560-1569.
- Gani, A., and Naruse, I. (2007). "Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass," *Renewable Energy* 32(4), 649-661.
- Haimour, N. M., and Emeish, S. (2006). "Utilization of date stones for production of activated carbon using phosphoric acid," *Waste Management* 26(6), 651-660.
- Hamada, J. S., Hashim, I. B., and Sharif, F. A. (2002). "Preliminary analysis and potential uses of date pits in foods," *Food Chemistry* 76(2), 135-137.
- Jenkins, B. M., Bakker, R. R., and Wei, J. B. (1996). "On the properties of washed straw," *Biomass and Bioenergy* 10(4), 177-200.
- Jensen, A., Dam-Johansen, K., Wojtowicz, M. A., and Serio, M. A. (1998). "TG-FTIR study on the influence of potassium chloride on wheat straw pyrolysis," *Energy Fuels* 12(5), 929-938.
- Karaosmanoglu, F., Cift, B. D., and Ergudenler, A. I. (2001). "Determination of reaction kinetics of straw and stalk of rapeseed using thermogravimetric analysis," *Energy Sources* 23(8), 767-774.
- Kastanaki, E., and Vamvuka, D. (2006). "A comparative reactivity and kinetic study on the combustion of coal-biomass char blends," *Fuel* 85(9), 1186-1193.
- Li, S., Xu, S., Liu, S., Yang, C., and Lu, Q. (2004). "Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas," *Fuel Processing Technology* 85(8-10), 1201-1211.
- Mansaray, K. G., and Ghaly, A. E. (1997a). "Physical and thermochemical properties of rice husk," *Energy Sources* 19(9), 989-1004.
- Mansaray, G. K., and Ghaly, A. E. (1999b). "Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis," *Biomass and Bioenergy* 17(1), 19-31.
- Manasray, G. K., and Ghaly, A. E. (1998c). "Thermal degradation of rice husks in nitrogen atmosphere," *Bioresource Technology* 65(1-2), 13-20.
- MNRE, (2009). *Booklets on Renewable Energy*, Ministry of New and Renewable Energy, (www.mnes.nic.in), 13, 777-88.

- Moghtaderi, B., Meesri, C., and Wall, T. F. (2004). "Pyrolytic characteristics of blended coal and woody biomass," *Fuel*, 83(6), 745-750.
- Pan, Y.G., Velo, E., and Puigjaner, L. (1996). "Pyrolysis of blends of biomass with poor coals," *Fuel* 75(4), 412-418.
- Park, W. C., Atreya, A., and Baum, H. R. (2010). "Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis," *Combustion and Flam* 157(3), 481-494.
- Peralta, D., Paterson, N., Dugwell, D., and Kandiyoti, R. (2002). "Development of a reactivity test for coal-blend combustion: The laboratory-scale suspension-firing reactor," *Energy Fuels* 16(2), 404-411.
- Rogner, H., and Abdel-Hamid, S. (2008). "Prospects for nuclear energy in west Asia and North Africa," *International Journal of Global Energy* 30(1-4), 162-176.
- Sensoz, S., and Can, M. (2002). "Pyrolysis of pine (*Pinus brutia* Ten) chips: 1. Effect of pyrolysis temperature and heating rate on product yields," *Energy Sources* 24(2), 347-55.
- Sharma, R. K., Wooten, J. B., Baliga, V. L., Lin, X., Chan, W. G., and Hajaligo, M. R. (2004). "Characterization of chars from pyrolysis of lignin," *Fuel* 83(11-12), 1469-1482.
- Steenari, B. M., and Lindqvist, O. (1997). "Stabilisation of biofuel ashes for recycling to forest soil," *Biomass and Bioenergy* 13(1), 39.
- Vamvuka, D., Kakaras, E., and Grammelis, P. (2003a). "Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite," *Fuel* (82), 1949-1960.
- Vamvuka, D., Kastanaki, E., and Lasithiotakis, M. (2003b). "Devolatilization and combustion kinetics of low-rank coal blends from dynamic measurements," *Industrial and Engineering Chemistry Research* 42(20), 4732-4740.
- Varhegyi, G., Jerry Antal Jr, M. J., Jakab, E., and Szabo, P. (1997). "Kinetic modelling of biomass pyrolysis," *Journal of Analytical and Applied Pyrolysis* 42(1), 73-87.
- World Energy Council (WEC). (2007). "Survey of Energy Resources," London.
- Zhao, H., Kwak, J. H., and Wang, Y. (2007). "Interactions between cellulose and N-methylmorpholine-N-oxide," *Carbohydrate Polymers* 67(1), 97-103.
- Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D. H., and Liang, D. T. (2006). "In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin," *Energy Fuels* 20(1), 388-393.
- Zickler, G. A., Wagermaier, S., Funari, S. S., and Burghammer, O. (2007). "In situ X-ray diffraction investigation of thermal decomposition of wood cellulose," *Journal of Analytical and Applied Pyrolysis* 80, 134-140.

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