

THERMOGRAVIMETRIC ANALYSIS AND KINETIC STUDY ON PALM OF PHOENIX DACTYLIFERA L.

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Abstract

Being an important date-producing country, Tunisia also has abundant wastes providing from the exploitation of date palm oasis, and these wastes can form a potential source of different forms of renewable energy through thermochemical conversion processes. However, an assessment of the use of these materials as a fuel requires a basic understanding of their composition, characteristics, thermal properties, and performance.

This work deals with the characterization of date palm leaflets (DPL) and rachis (DPR), two parts from palm of *Phoenix dactylifera* L., using thermogravimetry analysis (TGA) as a tool. First, the two samples were characterized by the proximate and ultimate analysis as well as heating value. Furthermore, laboratory tests were carried out by TGA to investigate different steps of thermal degradation of each sample at a heating rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$ under inert and oxidative atmospheres. Latter, kinetics parameters (activation energy (E) and pre-exponential factor (A)) were estimated. A two-step consecutive reaction model was used to simulate the weight loss during thermal degradation. This study is accomplished by comparing results belonging to date palm waste with other biomasses in literature.

Keywords: Date palm leaflets, Date palm rachis, Thermogravimetric characterization, Pyrolysis, oxidative pyrolysis.

Introduction

Utilization of agricultural or agro-industrial residues as an energy resource has various economical and environmental advantages such as reduction in the energy dependency on imported fuels and minimization of waste disposal. Tunisia has a considerable amount of biomass potential that could be used for energy production. Main sources of biomass include agriculture waste, such as olive waste, date palm waste. In fact, such lignocellulosic materials are available in large quantities and their use does not compromise food crops. Nevertheless, this biomass potential is mainly determined by the food development because production increases with increasing productivity of food.

Date palm (*Phoenix dactylifera*) is one of the most cultivated palm trees in many regions of the world. It has been one of the most important plants of arid, desert areas of northern Africa, the Middle East, and southern Asia. Cultivation of the tree has been spread from his native region to nearly all tropical and subtropical regions of the world.

The stem of the tree is unbranched and is covered by old remaining leaves or palms. New palms appear as a crown at the top of the stem. The two parts of palm are rachis which is the main axis and series of leaflets on each side of a common petiole. On a dry weight basis, in the whole palm the amount of leaflets is (46%) and rachis is (53.4%) [1]. An adult date palm

tree has approximately 100 to 125 green palms with an annual formation of 10 to 26 new leaves [2].

Palm trees are abundant in several regions in the south of Tunisia. Country palm plantations cover in area of 32 000 ha, approximately containing 4.2 million trees [3], with a production increasing from 86 050 tons during 1993–1994 company to 100 000 tons during that of 2005–2006. In 2003, 36.2% of Tunisian dates were exported, which represent 42 010 tons [4].

During date fruit harvesting important quantities of date palm waste are generated every year, such as date stones, empty bunches and palms. Unfortunately, few reliable data exist concerning the amount and no specific method is suitable for determining the standing volume or weight and yield for all these wastes. However, existing statistics tend to prove that the quantities are important and the main waste is the dry palms [5]. In addition, the usefulness of these agricultural wastes, as a fuel, will highly depend on their quality including properties that are important to assess its potential against the technologies to be deployed to use them efficiently and with low emission level.

Despite that these wastes are an attractive source of biomass energy, their valorization as renewable energy source is currently limited to traditional applications and few investigations were performed to assess their potential. In particular, Al Omari has examined the potential of date stones and palm stalks as an energy source for furnace over a wide range of experimental conditions in a small scale furnace with a conical solid fuel bed. Author has noted that these biomasses are technically a viable alternative in the heat generation installations [6, 7].

Thermogravimetric analysis (TGA) is one of the main techniques used for the study of thermal behaviour of carboneous materials and kinetics of the thermal decomposition reactions. This technique is also interesting for the analysis of biomass wastes. The rate of weight loss of the sample as a function of temperature and time is measured to predict thermal behaviour of the material. Several papers dealt with the thermal characteristics of different biomasses [8, 9]. However, there has been no report about the kinetic studies of date palm solid waste in the literature and they have not yet been compared with conventional biomasses from a thermal behaviour perspective.

The purpose of this work was to characterize palm parts of date palm tree intended as feedstock for use in pyrolysis and combustion processes for converting them into usable energy or material products. TGA techniques and other characterization tests have been used to evaluate the thermal behaviour under inert and oxidizing atmospheres of both date palm leaflets (DPL) and rachis (DPR). Moreover, the kinetic parameters have been provided using different kinetics models currently used to describe biomass thermal degradation. Experimental results may provide useful data for the design of oxidative reaction and pyrolysis processes using date palm waste as feedstock.

Materials and methods

Sample preparations

Date palm wastes were provided from different varieties accumulated in south of Tunisia. Palms used in this study were collected from an oasis in Tozeur in April 2010. The leaflets were separated manually from the rachis. Then, DPR were grounded in order to have homogeneous products. The two wastes were dried under natural conditions during 2-3 days in order to reduce water content. DPL were cut to 1-2 cm in width and 4-5 cm in length. After sieving, one size of DPR was selected for tests with particle diameter ranging from 1 to 2 mm.

Sample characteristics

Before thermogravimetric analysis, the samples were analyzed to determine the main properties that affect thermal behaviour. Proximate analysis measurements were conducted using a thermogravimetric analyser (CAHN 121 thermobalance). Proximate TG method involves the heating of the sample (under N₂) at a rate of 10°C/min from room temperature to 110 °C and then holding for 60 min to obtain the weight loss associated with moisture. Temperature is then ramped from 110 °C at a rate of 20°C/min to 900 °C (under N₂) and held for 30 min to obtain weight loss associated with volatiles release. Oxygen is then introduced into the furnace chamber to oxidize the carbon in the char and the weight loss associated with this defines the fixed carbon. The remaining material after oxidative pyrolysis is the ash. On the other hand, ultimate analysis corresponding to elemental compositions of the two samples (C, H, N, S contents in the four samples) was done by Service Central d'Analyses (Vernaison, France). Finally, heating values of the four fuels were measured using an adiabatic oxygen bomb calorimeter (Prolabo).

Thermogravimetric experiments

For the determination of the thermal degradation characteristics of the two materials, dynamic experiments have been done under inert nitrogen and air (20% O₂ and 80% N₂) conditions using a CAHN 121 thermobalance. A constant gas flow of 12Nl/h is used to feed the system in all the tests with heating rate of 5 °C/min from room temperature to 900 °C. Initial samples weighing approximately 10 mg were placed in a hemispherical crucible of 4 mm deep and 9 mm diameter at its mouth. The use of small masses was necessary to limit the side reactions as well as mass and heat transfer [10]. For each experimental point, the reproducibility was checked by at least a duplicate run.

Kinetics approach

Several approaches of the kinetic analysis of non-isothermal TGA data have been used for the determination of the reactivity parameters for biomass thermal degradation. The kinetic analysis of dynamic results involves attempting to relate the experimentally observed values of conversion rate of sample masse against temperature with values predicted for a limited set of models based on process of nucleation and growth, diffusion or some simpler geometrical forms of progress of the reactants / product interfaces [11].

In order to determine kinetic parameters of the two parts of *P. dactylifera* palm, kinetic schemes were studied accordingly to literature data [9, 11].

The rate of decomposition reaction can be expressed by the following equation when the Arrhenius equation is chosen:

$$\frac{d\alpha}{dt} = Kf(\alpha) = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

Where $\alpha = (w - w_f) / (w_0 - w_f)$ is the degree of transformation of the sample (w is the mass at any time and subscripts 0 and f respectively refer to the initial mass and final mass at the end of that stage) and t is time. $f(\alpha)$ represents function commonly used for description of biomass thermal decomposition. K is the reaction rate constant, A the frequency factor, E the activation energy, R the gas constant and T the absolute temperature. For the non-isothermal condition with a heating rate ($q = dT/dt$), Eq. (1) can be rewritten as follows:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{q} \exp\left(\frac{-E}{RT}\right) dT \quad (2)$$

Integrating equation (2), the following expression can be obtained:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{q} \int_0^T e^{(-E/Rt)} dT \quad (3)$$

We can integrate the last equation when the right hand side is expanded into an asymptotic series and higher order terms are ignored.

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left\{\frac{AR}{qE} \left[1 - \frac{2RT}{E}\right]\right\} - \frac{E}{RT} \quad (4)$$

In general, the term $2RT/E$ can be neglected since it is much less than unity for the thermal decomposition of lignocellulosic materials. A plot of $\ln[g(\alpha)/T^2]$ against $1/T$ will give a straight line of slope $-E/R$ and an intercept of $\ln(AR/qE)$ for an appropriate form of $g(\alpha)$. Thus, based on the correct form of $f(\alpha)$, the activation energy and the pre-exponential factor can be determined respectively from the slope and intercept terms of the regression line.

Table 1 lists the functions $f(\alpha)$ and $g(\alpha)$ used in this work to describe biomass thermal decomposition. Thus, two models which have been developed based on certain mechanistic assumption are proposed to interpret experimental data for both oxidation and pyrolysis. They can be classified into two categories:

- Reaction order: the rate law is based on the reaction order.
- Diffusion mechanisms: the rate limiting step is the diffusion of the reactants into reaction sites or products away from reaction sites.

Table 1. Kinetic mechanism function.

Model	$f(\alpha)$	$g(\alpha)$
Reaction order		
O0	1	α
O1	$(1-\alpha)$	$-\ln(1-\alpha)$
O2	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$
O3	$(1-\alpha)^3$	$(1-\alpha)^{-2} - 1$
Diffusion mechanisms		
D1	$1/(2\alpha)$	α^2
D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	$3/2[(1-\alpha)^{-1/3} - 1]^{-1}$	$(1-2\alpha/3) - (1-\alpha)^{2/3}$

Results and discussion

Raw materials characteristics

Table 2 presents the results of characteristic properties obtained for the two samples regarding their proximate and ultimate analysis, heating values and bulk density. Analysis findings

show that these wastes have acceptable heating value compared with wood [8] and high content of volatiles, carbon, hydrogen and oxygen. Together, heating value and bulk density establish the energy density that is the potential energy available per unit of biomass. Relative contents of sulphur and nitrogen are low compared to C, H and O. Therefore, according to Loo and Koppejan, emissions of sulphur and nitrogen oxides from these materials would be minimum [12]. In all cases, these results are in the same order of magnitude than the typical composition of biomass [13].

For the proximate analysis, DPL presents a high value of ash content. This value may influence the oxidative process.

Table 2. Proximate and ultimate analysis.

waste	Proximate analysis (%) ^a				Ultimate analysis (%) ^a						
	Moisture	VM	FC	Ash	C	H	O	N	S	HHV ^a (MJ.kg ⁻¹)	BD ^a (kg/m ³)
DPL	07.1	68.0	9.7	15.2	40.8	6.0	35.2	0.63	0.21	17.6	312
DPR	12.1	73.6	8.3	6.0	39.8	5.7	43.0	0.19	0.26	15.9	173

a= as-received basis

VM = volatile matter, FC = fixed carbon, HHV = high heat value, BD = bulk density.

Analysis of the thermograms

Thermal conversion of lignocellulosic materials is complex due to the different degradation behavior of major constituents, i.e. cellulose, hemicellulose and lignin, interactions between constituents, and effects of minute amounts of mineral matter naturally present in whole biomass samples [14]. Information concerning chemical composition of the samples is reported in Table 3. The chemical composition of samples is roughly the same.

Table 3. Chemical composition of leaflets and rachis.

Constituent	Ash	Hemicelluloses	Cellulose	Lignin
Leaflets ^a	6.5	26	33	27
Rachis ^a	2.5	28	44	14

a= according to [1].

Thermal degradation under inert atmosphere

Based on the mass loss (X) obtained by thermogravimetric analysis (TGA) during the pyrolysis of the two lignocellulosic materials, the calculated derivative of mass loss (dX/dt) curves, or derivative thermogravimetric (DTG), could be obtained. Figure 1 shows both X and dX/dt curves for the different tested sample at 5°C/min. The thermal degradation of lignocellulosic materials under inert atmosphere was well described in the literature [8-10].

According to these figures, pyrolysis curves of palm parts follow the usual shape for lignocellulosic materials [15]. Indeed, the following curves show the typical degradation profile with well demarked regions for moisture release, devolatilization and char degradation. The first mass loss region due to moisture release and light volatiles loss occurs between 25°C and 150°C. The apparently higher moisture release from DPR could be due to simultaneous moisture and low temperature volatiles release. Then, devolatilisation, which is the main pyrolysis of lignocellulosic materials, starts at proximately 180°C and 160°C for DPL and DPR, respectively. Such variations in initial degradation temperatures of biomasses

have been related to the differences in the elemental and chemical compositions of the samples [17]. There were major weight loss (where the main degradations occurred), which ended at approximately 367°C and 333°C for the same sample sequence. During the devolatilization step, two decomposition processes corresponding to the degradation of hemicellulose and cellulose are observed. For the pyrolysis of DPL and DPR, there are two distinct regions of DTG curves. The first region appears as a more or less pronounced shoulder at approximately 238°C and 210°C for DPL and DPR respectively. However, the following second region is characterized by peaks with maxima at 315°C and 297°C, for the two samples respectively. Appearance of shoulders could be generated by the decomposition of hemicellulose and some of the lignin. The peak should correspond to the decomposition of cellulose and the remaining of lignin. When hemicellulose and cellulose decompositions overlap, the shoulder marks the peak top of the hemicellulose decomposition [16]. At the end of this decomposition step, a continuous slight devolatilization is observed. This is attributed to the slow degradation of lignin [17]. Thus, lignin is the first component to decompose at a low temperature and low rate and continues up to 900 °C.

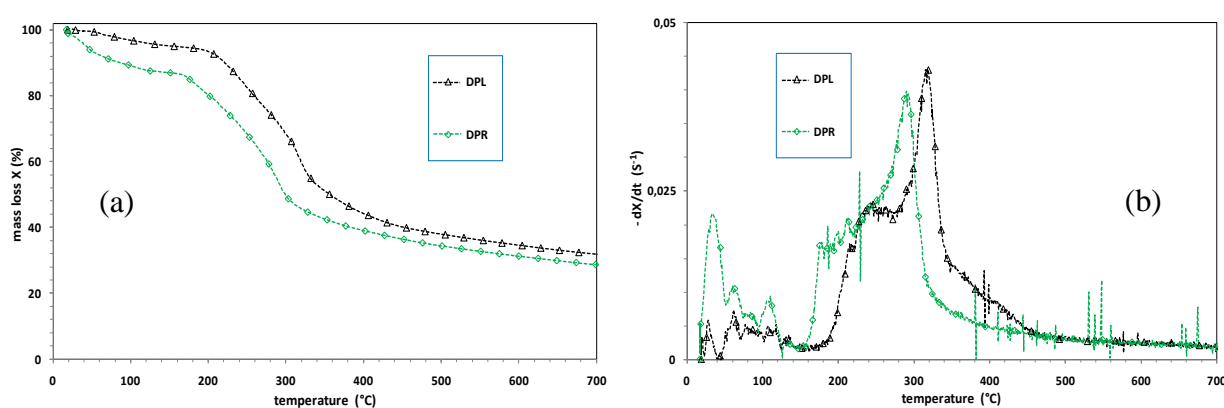


Figure 1. TGA (a) and DTG (b) curves of the experiments performed under nitrogen.

Rate of mass loss as indicated by the DTG is an indication of reactivity of the material. Hence, it is observed that the rate of decomposition of the heavy component is dominated for both DPL and DPR. The maximum rates of weight loss (% s⁻¹) were 0.043 and 0.039 for DPL and DPR respectively. These last values were higher compared to other biomasses tested by Grønli et al. as well as Jeguirim, and Trouvé in the same experimental conditions [15, 18]. However, they were quite similar than the ones obtained for olive oil mill wastewater and sawdust samples [19].

Thermal degradation under oxidative atmosphere

TGA and its DTG of DPL and DPR under air atmosphere at the heating rate of 5°C/min are plotted against the temperature in the Figure 2. (a) and (b).

As can be observed in these curves, weight losses present three main steps: the first accounts for moisture evaporation, the second is due to devolatilization and the last relates to the oxidation of char.

The first stage in the oxidizing atmosphere ranged from room temperature to 125°C. It was similar to the first stage in the inert atmosphere. Loss of water and volatilization of light molecules may have contributed to weight loss in this stage. Thus, the second stage of weight loss occurs at temperatures between 175°C and 340 °C. It is noted that the two maximum of decomposition rates occur at about 304°C and 264 for both DPL and DPR respectively.

At the end of oxidation, residual mass of DPL is about 14.5% of the initial mass which is higher than the ash obtained for DPR (7.1%). In addition, it should be noted that a fuel with a higher percentage of ashes and impurities in its composition, presents a lower initial temperature of degradation [14].

As evidence from DTG curves in Figure 2. (b), a close similarity is shown for the two samples during char oxidation phase. This region proceeds between 370°C and 424°C for both DPL and DPR.

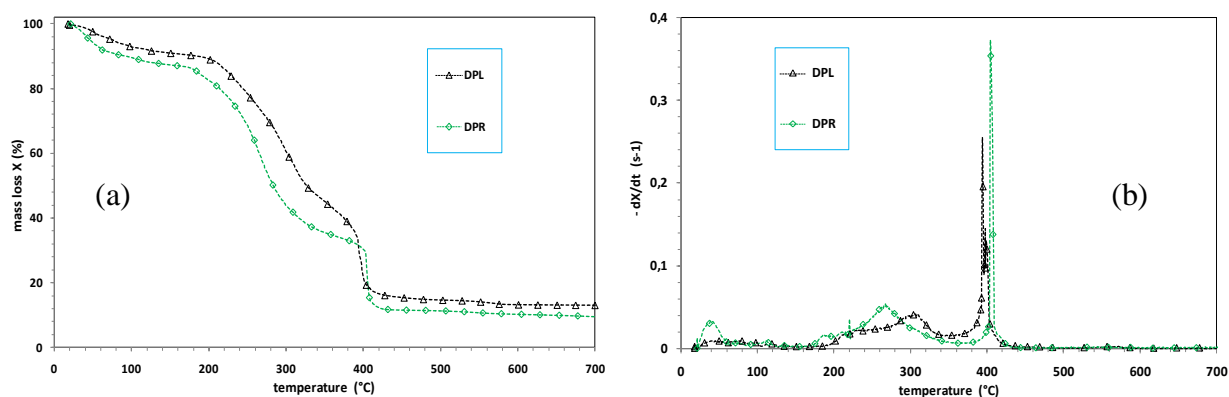


Figure 4. TGA (a) and DTG (b) curves of the experiments performed under air.

Kinetic parameters

Using data from the pyrolysis thermograms (Figure 3.), the kinetic parameters at two temperatures regimes were computed by using two different methods (based on reaction order or based on diffusion mechanisms) which give best fit of experimental results. The kinetics parameters (pre-exponential factor, activation energy) and the correlation coefficient for the two samples during pyrolysis are given in Table 4. The temperature ranges for the two regression calculations are also reported.

As shown in Table 4, the used method has effects on the activation energy and frequency factor calculated for both high and low pyrolytic regimes. The values of correlation coefficients and the temperature ranges for the two regression calculations can be used to compare results obtained by the two models.

For low temperature regimes, it can be seen that the models based on diffusion mechanisms lead to a much better fit of experimental data than the models based on reaction order. Moreover, diffusion mechanism models can be used for a largest temperature ranges for regression calculation. However, for high temperature regimes, the models based on reaction order give the best fit of experimental data.

It can be inferred from the last discussion that in the low and high temperature regimes, the models based on diffusion mechanisms and the models based on reaction order can be used to describe the pyrolysis kinetics of our biomass respectively. This is in accordance with Guo and Lua who determined the kinetic parameters on pyrolysis of extracted oil palm fiber [9].

Table 4. Kinetic parameters for mass loss of DPL and DPR under pyrolysis.

Sample	Temperature regime	Masse loss temperature range °C	Activation energy E(KJ.mol ⁻¹)	Frequency factor lnA (s ⁻¹)	R	Method used
DPL	Low temperature	174°C-376°C	63.03	3.47	0.9908	D3
		179°C-376°C	39.29	1.37	0.9905	O2
	High temperature	376°C-440°C	13.25	-7.64	0.9907	D3
		376°C-450°C	39.80	3.02	0.9989	O3
DPR	Low temperature	163°C-328°C	31.56	-1.25	0.9966	D1
		163°C-328°C	11.77	-5.92	0.9965	O3
	High temperature	328°C-381°C	3.18	-11.08	0.9514	D4
		328°C-587°C	19.20	-1.23	0.9984	O3

The kinetic parameters of each sample during devolatilization step under oxidative atmosphere are shown in Table 5. In this initial stage, for DPL and DPR, a two-dimensional and a three-dimensional diffusion mechanisms respectively were found to best describe the weight loss kinetics.

Table 5. Kinetic parameters of DPL and DPR under oxidative pyrolysis

Sample	Temperature regime	Masse loss temperature range °C	Activation energy E(KJ.mol ⁻¹)	Frequency factor lnA (s ⁻¹)	R	Method used
DPL	Devolatilization	185°C-351°C	45.94	1.55	0.9824	D ₂
		200°C-348°C	4.15	-6.54	0.9803	O ₁
DPR	Devolatilization	175°C-330°C	57.91	2.45	0.9903	D ₃
		175°C-330°C	23.61	-2.42	0.9738	O ₁

Conclusions

Thermogravimetric behaviour of the two parts of *P. dactylifera* palm was examined at heating rate of 5°C/min in both nitrogen and oxidative atmosphere using a thermogravimetric analysis technique. Furthermore, chemical composition, heating values and bulk density of the samples were examined to assess their suitability for potential use as biofuel and or for further processing to produce activated carbons. Also, data from thermogram were analyzed to determine the main characteristics of thermal degradation. On the other hand, the trend of the TGA, and DTG, curves were evaluated to obtain information on reactivity of the samples and to simulate the pyrolytic process and devolatilization step on the oxidative pyrolysis by predicting the kinetic parameters.

The data obtained from this study are useful for preliminary assessment of date palm waste as a feedstock for thermochemical conversion systems.

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