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Pyrolysis behaviour study of date palm biomass in Algerian oasis using thermogravimetric analysis.Deglet Nour cultivar case

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***Abstract*— The objective of this work is the study of the thermal behavior, under an oxidative atmosphere of the phoenicicole biomass main constituents related to the dominant cultivar, Deglet Nour (DN). Thermogravimetric analysis (TGA) is the approach used to study the pyrolysis behavior of this lignocellulosic biomass, the determination of the kinetic constant (activation energy, order of the reaction, pre-exponential factor), the description of different thermal profile.The statistical method used for the examination of the TGA data are the analysis of variance ANOVA and principal component analysis PCA.**

The results show that pyrolysis process could be an interesting alternative energy recovery for the phoenicicole biomass. This is explained by the low activation energy which is estimated on the average at 28.78 k J/mol. For the whole studied biomass, kinetic, thermal and chemical parameters are advantageous in comparison with conventional solids biofuels. An exception was observed for Lif part which is unsuitable for pyrolysis process because of its thermal stability.

Keywords-Phoenicicole biomass; Thermogravimetric; Kinetics; Pyrolysis ; Classification

I. INTRODUCTION

Biomass is a sustainable alternative to the numerous planetary preoccupations related to climate change in general and greenhouse gases in particular [1]. It has many advantages that make it competitive or even preferred over other renewable energy i.e.: a very substantial deposit (especially lignocellulosic resources), a zero carbon footprint, a waste recycling...[2] In the Oasis context, the date palm (*Phoenix dactylifera L.*) could be considered an attractive and sustainable energy source since it offers many advantages (biochemical, ecological, socio-economic, environmental ...) [3-10]. The thermal behavior study of this biomass is an essential step for an initial evaluation of its energy quality [1, 7].

In recent years, many technologies have been the subject of studies on the potential energy uses of biomass. This is precisely the case of pyrolysis which is very promising in this field. The study of this latter, appears to be necessary and a priority because it is a precursor process for all chemical thermoconversions (Combustion, gasification, liquefaction ...) [11]. However, the biomass pyrolysis is a very complex process, governed by a series of reaction which kinetics is influenced by multiple factors: physical type of biomass, heat transfer and mass, operating conditions (Heating rate, gas flow ...). At an analytical level, we add to these factors the analysis methodology and the equipment used[12].

Thermogravimetric analysis (TGA) is one of the most commonly used analytical techniques for the study of the biomass thermal behavior under pyrolysis. It is a simple and rapid method based on the determination of the weight change depending on the temperature; and that essentially considers the weight, temperature and time. The interpretation and exploitation of the curves obtained require the drawing of the derivative thermogravimetric DTG. The determination of kinetic parameters responsible for the prediction of the biomass thermal behavior is based on the application of the Arrhenius model. However, the low heating rate (important run time) and the need to use small amounts (representability problem results) are, limitations to this technique [1, 9, 13-15].

The choice of phoenicicole biomass for this study is based on several reasons. The first one is its chemical quality compatible with that of conventional biofuels [6, 7]. The second reason is the scarcity of studies in the chosen thermal conversion field [6-9]. The third reason is the importance of biomass deposit in the Algerian oasis especially cultivar selected for this study. This last one represents 40% of Algerian phoenicicole park and generates significant amounts of residues (65 kg / tree / year) [4, 6, 16].

In summary, this work aims the study of the phoenicicole biomass kinetics, under slow pyrolysis (10 °C / min), corresponding to DN cultivar, using the TGA. Two statistical analyses (analysis of variance and principal component analysis PCA) were used to allow the interpretation of the results. Thus, this study will enable us to answer and address the following research questions:

What is the thermal behavior of the phoenicicole biomass related to DN cultivar, under pyrolysis process? What are the kinetic (activation energy, order of the reaction, pre-exponential factor) and the thermal characteristics (onset and offset devolatilization temperature) of the phoenicicole biomass related to DN cultivar? What are the most interesting phoenicicole biomass constituents, related to DN cultivar, for pyrolysis process?

The area chosen for the realization of this study is the Guerrara oasis (Algeria - Latitude: 32 ° 47 ' North Longitude: 4 ° 30 East), which served as a model for the study of biomass deposit at the regional (Mzab) and national level (Algerian oasis) [4, 6, 16].

II. MATERIALS AND METHODS

A. *Methods of sample preparation and chemical composition*

Sampling, sample preparation and analysis (proximate, ultimate and calorimetry) were conducted according to the standards described in [6].

B. *Thermogravimetric Analysis*

The TGA is carried out in SETARAM Setsys Evolution 16/18 Thermogravimetric analyzer. The specification and test conditions of the Thermogravimetric analyzer are presented in Table I.

TABLE I. SPECIFICATIONS AND TEST CONDITION OF THERMOGRAVIMETRIC ANALYZER

Model Balance sensitivity	Setsys Evolution 16-18 (model with integrated controller CS32)
Balance accuracy	0.4 µg
Maximum weight	200 mg
Temperature range	25 to 1600°C
Heating and cooling rates	0.1 – 200 °C/min in 0.1 increments
Type of sample	Solids, liquids, powders, films or fibers
TGA atmosphere	Static or dynamic including nitrogen, argon, carbon dioxide, air, oxygen or other inert or active gases
Temperature sensors	S type thermocouple with 10% rhodium platinum
Heating rate	10°C/min
Purge gas	N_2
Purge gas rate	200 ml/min
Initial temperature of the sample	25.00 °C
Final temperature	600 °C

C. *Kinetic parameters*

Thermogravimetric analysis (TGA) leads to the thermal characterization (chemical kinetics) of the biomass by direct measurement of their mass as a function of the temperature and (or) time. This chemical kinetics of different thermochemical conversions (pyrolysis, combustion or gasification) combined with other parameters (chemistry) can provide the necessary information for the understanding and optimization of these processes [17]. Several additional techniques are used in parallel at the TGA for the determination of kinetic parameters (differential thermal analysis DTA ...).

Bibliographical references mention several studies and methods for the determination of kinetic parameters [9, 12, 15, 18-22] ; that used for our case is based on the FRIEDMAN model [23]. All these kinetic models are based on the Arrhenius equation given by:

$$d\alpha/dt = A \exp[(-E)/RT]\,(1-\alpha)^n \qquad (1)$$

Where: $d\alpha/dt$, A, n, E, R, α, T, t are respectively the conversion rate, the pre-exponential(s^{-1}), the order of reaction, activation energy (kJ/mol), the universal gas constant, the fraction of reactant decomposed at time t (%), the absolute temperature (°K) and the time (s).

Given that:

- The mathematical form of the conversion α can be written as :

$$\alpha = (w_0 - w) / (w_0 - w_f) \qquad (2)$$

- The constant heating rate β, is given by :

$$\beta = dT/dt \qquad (3)$$

Where: w, w_0 and w_f are respectively the weight of the sample at a particular time t, its initial and final weight.

The equation (1) is written:

$$d\alpha/dT = A/\beta\ \exp[(-E)/RT](1-\alpha)^n \qquad (4)$$

$$d\alpha / (1-\alpha)^n = A/\beta\ \exp[(-E)/RT]dT \qquad (5)$$

Considering some approximations:

- Rearrangement and integration of equation (5)
- Approximation of the order of the reaction to the unity

The equation (5) becomes:

$$-\ln(1-\alpha) = A/\beta.[(R.T^2)/E] \exp[(-E)/RT)] \qquad (6)$$

$$\ln[-\ln(1-\alpha)] = \ln[A/\beta.(R.T^2)/E] - E/RT \qquad (7)$$

This equation is of the form:

$$y = b + ax \qquad (8)$$

Where:

$y = \ln[-\ln(1-\alpha)]$; $b = \ln[A/\beta.(R.T^2)/E$; $a = -E/R$; $x = 1/T$

The constant a is estimated by simple linear regression data obtained from the TGA on the major interval devolatilization of the biomass studied. Microsoft Excel was used for these calculations. The results obtained, namely the activation energy E and R^2 regression coefficient, are shown in Fig. 2 and Table II.

D. Principal compnent Analysis PCA

The Principal Component Analysis (PCA) was applied to:

- Thermal parameters which includes: onset and offset devolatilization temperatures of pyrolysis (T_{onset} and T_{offset}), the corresponding activation energies, the yield (ΔMass) of the thermochemical process and the calorific value of biomass (HHV).
- Chemical parameters which includes: proximate parameters (fixed carbon FC, volatile matter VM and ashes A). The moisture parameter was not taken in account for the PCA because of its low variability.

III. RESULTS AND DISCUSSION

A. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the date palm residues (DN cultivar case) performed under an inert atmosphere at 10°C/min, represents derivatives DTG mass depending on the temperature (Fig. 1). These curves show the main phases of the pyrolysis process related to the phoenicicole biomass and identify their thermal degradation profile:

- The **first phase** corresponds to the dehydration of the biomass i.e. the elimination of the moisture (between 100°C and 130°C) and the light volatiles matters (. It happens in a temperature range comprised between 31 and 198°C. Water is eliminated between 100°C and 130°C while light volatiles matters are extracted from 130°C to 250°C.
- The **second phase** is characterized by an important degradation of biomass. The second step of degradation is known as active pyrolysis zone where volatilization is at its maximum. In this stage, there is an intermolecular association and breaking chemical bonds. Due to the low temperatures, aliphatic side chains can break and small gas molecules form. Furthermore, the totality of volatiles is removed in this interval. It happens in a temperature that ranges between 198°C and 391°C on average. This phase also corresponds to the degradation of hemicellulose (250-350 °C) and cellulose (250-500 °C). For lignin this range is between 360-400 °C [24].
- The **third phase** is characterized by the slow degradation of the remaining materials (char). In this interval (391°C and 600°C), the chemical bonds associated with higher temperatures can break and the compounds with high molecular weights are converted into small compounds molecular weight. This phase concerns essentially the degradation of lignin whose decomposition temperature is between 280°C and 450°C, and may exceed 500°C due to its thermal stability related to the phenolic hydroxyl group. The formation of a char characterizes the end of this phase [24].

Fig. 1 shows also the variation of the thermal behavior between biomass components translated by the variation of the temperature ranges. This can be explained essentially by the difference in the phoenicicole biomass composition especially on mineral level [6, 25, 26].

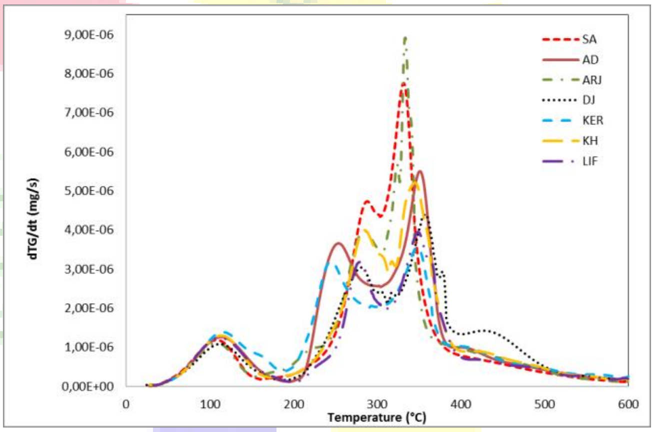

Figure 1. Typical dTG diagrams of the phoenicicole biomass related to the DN cultivar under inert atmosphere

B. Kinetic parameters

In order to simplify the interpretation and the exploitation of the thermograms, the interval considered for the calculation of the kinetic parameters is the one where the thermal decomposition process is the most important (maximum degradation rate). This calculation allowed to reach significant correlation coefficients R^2 (Fig. 2 and Table II). Indeed, for pyrolysis process, this rate varies between 0.93 and 0.99, an average of 0.97.

Table II and Fig. 3 show the pyrolysis kinetic parameters (activation energy, reaction order and pre-exponential factor) of the phoenicicoles main residues related to Deglet Nour cultivar in the Guerrara oasis.

A general observation of the activation energy (Table II and Fig. 3) related to the phoenicicole main constituents (DN cultivar case) shows there is no significant variation of this parameter among different wastes. The average value is estimated at 28.78 kJ/mol (palm case). The energy d'activation varies between 26.71 kJ/mol (petiole case) and 32.46 kJ / mol (spathe case). On the basis of this parameter, we can say that the petiole (KER) appears slightly more advantageous than the remaining biomass study for pyrolysis process.

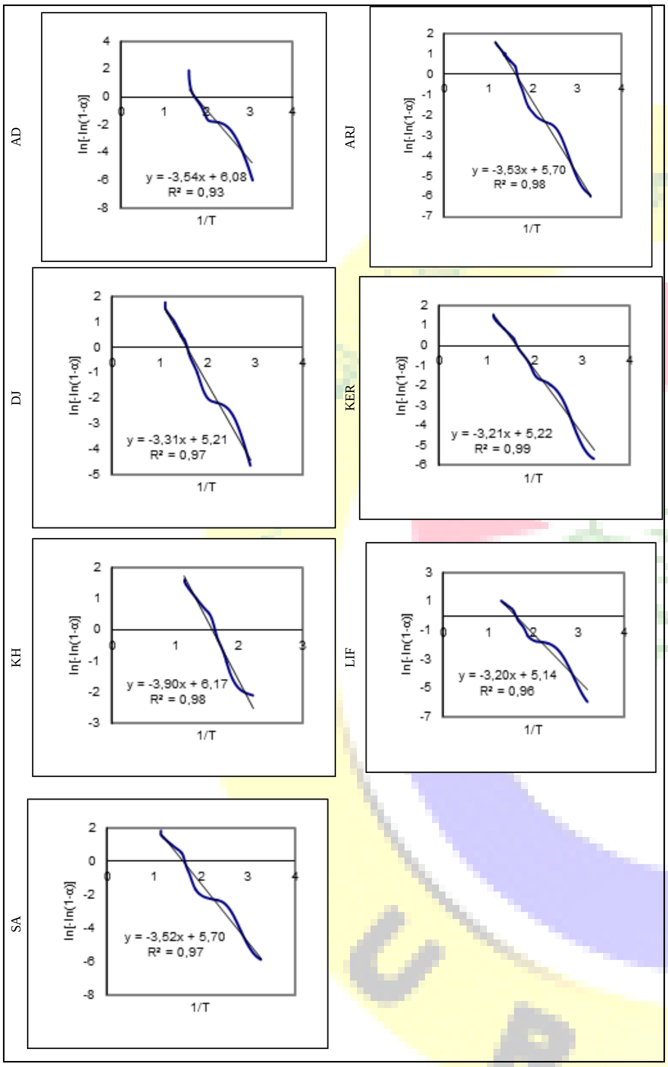

Figure 2. Kinetic plots for the phoenicicole biomass (DN Cultivar case) under inert atmosphere at 10°C/min

The order of the reaction (n) is estimated to be about 0.87 (SA) on average for the whole studied biomass. It varies between 0.58 (LIF) and 1.47 (ARJ).

The pre-exponential factor varies very significantly between 1.70 s^{-1} and 648229.45 s^{-1} for the pyrolysis process.

TABLE II. KINETIC PARAMETERS OF PHOENICICOLE BIOMASS (DN CULTIVAR CASE) UNDER INERT ATMOSPHERE

Biomass	Linear regression		Regression coefficient	Activation energy	Pre-exponential factor	Reaction order
	b	a	R^2	E (kJ/mol)	B = ln(A)	n
AD	- 3.54	6.08	0.93	29.43	11.21	1.18
ARJ	-3.53	5.70	0.98	29.32	13.38	1.47
DJ	-3.31	5.21	0.97	27.55	1.32	0.68
KER	-3.21	5.22	0.99	26.72	1.58	0.65
KH	-3.90	6.17	0.98	32.46	2.46	0.70
LIF	-3.20	5.14	0.96	26.61	0.53	0.58
SA	-3.52	5.70	0.97	29.29	2.30	0.81

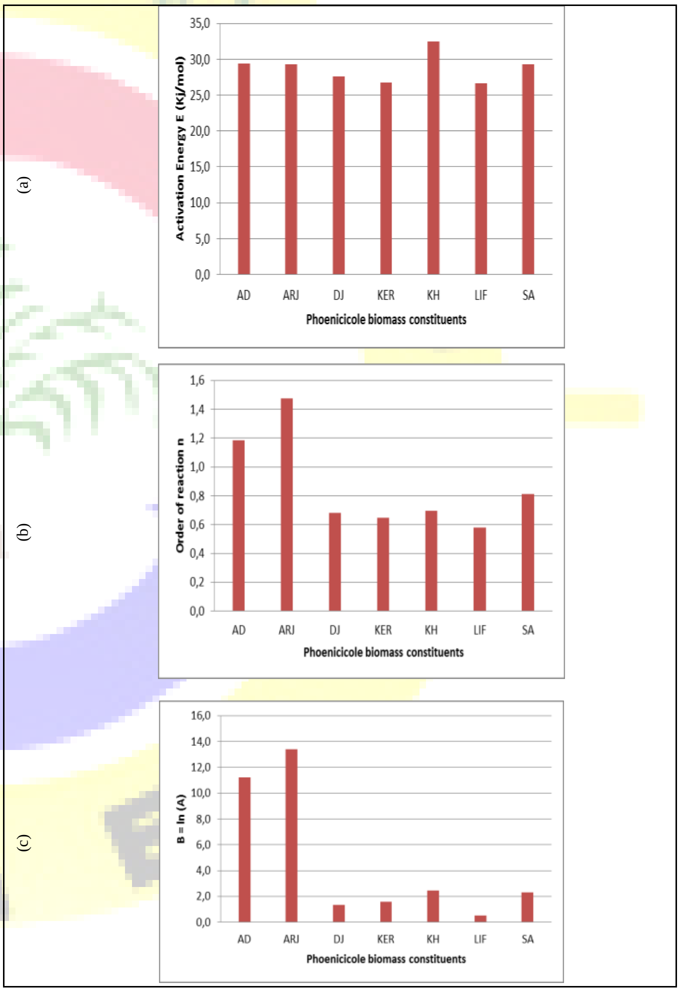

Figure 3. Kinetic parameters of phoenicicole biomass (DN Cultivar case) under inert atmosphere at 10°C/min
a : Activation Energy ; b : Ordre of the reaction ; c : pre-exponential factor

C. Classification of the main phoenicicole biomass

Four categories of the studied biomass were identified after the principal component analysis according to the settings mentioned above (see Fig. 4):

The **first group** represents the LIF sample of DN cultivar; it is characterized by high ash content (~ 16%), fixed carbon (~ 29%) and cellulose content (50.6%. This group is characterized by thermal stability mainly due to the high lignin content. This explains the high devolatilization temperatures (195.46 °C and 394.50 °C respectively), the low calorific value (15 MJ/kg) and low conversion rate (55%).

The inflorescence part (fruit stalk pruning (SA) and fruit bunch (ARJ) spathe (KH)) represents the **second group.** In contrast to the first group (on the plane symmetrical), the second is characterized by a high thermal reactivity explained by a high content of hemicellulose and a low ash (~ 8%). This explains the high calorific value (20 MJ/kg) and an elevated pyrolysis yield (70%). Moreover, the initial and final temperatures of devolatilization (153 – 376 °C) are relatively low in comparison to the previous group.

The **third group** represents the basal part of the palm (AD and KER) and the spathe (KH) corresponding to DN cultivar. This group is characterized by intermediate values for all parameters (energetic and chemical) with the exception of the activation energy and high heating value, which are respectively estimated on average at 29 kJ / mol and 19 MJ / kg and are relatively high compared with other samples.

The palms (DJ) constitute the **last group** (fourth) which is characterized by almost equivalent cellulose and hemicellulose content, very high ash content (~19%), a significant calorific value (20 MJ / kg). these elements explain a high pyrolysis yield (69%).

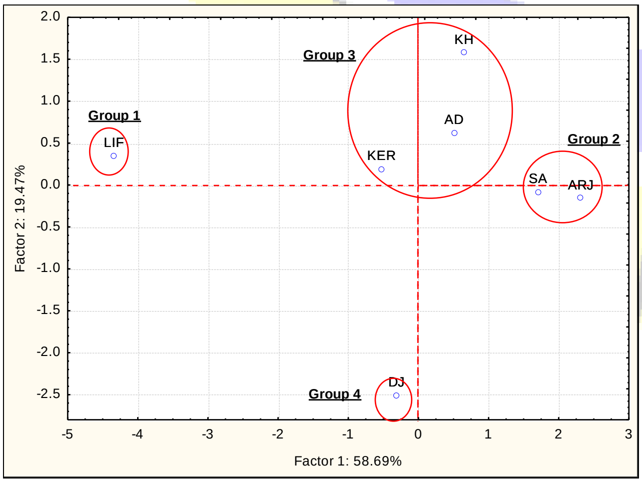

Figure 4. Projection of variables on the factor-plans (1 x 2)

IV. CONCLUSION

Thermogravimetric analysis TGA was carried out to study thermal behavior of the phoenicicole main constituents related to Deglet Nour cultivar considering pyrolysis process. The approach used is based on the calculation of the kinetic parameters (activation energy. reaction order and pre-exponential factor), the review of the different thermal characteristics related to the biomass decomposition phases and the classification of studied biomass taking into account energetic and chemical parameters.

The thermal profile of the phoenicicole biomass is characterized by three decomposition stages corresponding to: dehydration, degradation of hemicellulose and cellulose and finally degradation of lignin which behaves as a thermal stabilizer.

In spite of invariability for the pyrolysis activation energy among different phoenicicole constituents, four groups were identified on the basis of their thermal behavior and chemical composition. The two characteristics categories are: firstly, the Lif part is inappropriate to a thermal conversion in an inert atmosphere because of its thermal stability due to the high content of lignin and ash. Secondly, the inflorescence part which may favor such thermoconversion thanks to a high thermal reactivity of dominant constituent i.e. hemicellulose and the low ash content.

REFERENCES

[1] M. V. Gil, D. Casal, C. Pevida, J. J. Pis, and F. Rubiera, "Thermal behaviour and kinetics of coal/biomass blends during co-combustion," *Bioresour Technol*, vol. 101, pp. 5601-8, Jul 2010.

[2] P. McKendry, "Energy production from biomass (part 1): overview of biomass," *Bioresource Technology*, vol. 83, pp. 37-46, 5// 2002.

[3] K. Bousdira, "Environmental approach of the Algerian oasis biomass energy conversion. Mzab area case," presented at the 18th European Biomass. Conference & Exhibition. From Research to Industry and Markets, Lyon France, 2010.

[4] K. Bousdira, "Eléments sur la valorisation énergétique de la biomasse oasienne algérienne," presented at the INWOP10, El Oued Algérie, 2010.

[5] K. Bousdira, L. H. Nouri, J. Legrand, A. Herma, A. Elmegbed, B. Djani, and N. Bendaoud, "Evaluation of the potential phoenicicol biomass sub-product in the Guerrara oasis " presented at the SIENR2012. The 2nd International Seminar on New and Renewable Energies, Ghardaïa – Algérie 2012.

[6] K. Bousdira, L. h. Nouri, and J. Legrand, "Chemical Characterization of Phoenicicole

Biomass Fuel in Algerian Oasis: Deglet Nour and Ghars Cultivars Case," *Energy & Fuels*, vol. 28, pp. 7483-7493, 2014.

[7] K. Bousdira, F. Z. Yahiaoui, S. M. E. A. Bekkouche, and B. Dina, "Pyrolysis kinetics of date palm biomass in Algerian oasis using Thermogravimetric Analysis. Ghars cultivar case," in *Third International Renewable and Sustainable Energy Conference (IRSEC'15).* Marrakech – Ouarzazate, Morocco, 2015.

[8] Y. Elmay, M. Jeguirim, S. Dorge, G. Trouvé, and R. Said, "Study on the thermal behavior of different date palm residues: Characterization and devolatilization kinetics under inert and oxidative atmospheres," *Energy*, vol. 44, pp. 702-709, 2012.

[9] H. H. Sait, A. Hussain, A. A. Salema, and F. N. Ani, "Pyrolysis and combustion kinetics of date palm biomass using thermogravimetric analysis," *Bioresour Technol*, vol. 118, pp. 382-9, Aug 2012.

[10] M. Mallaki and R. Fatehi, "Design of a biomass power plant for burning date palm waste to cogenerate electricity and distilled water," *Renewable Energy*, vol. 63, pp. 286-291, 2014.

[11] P. Parthasarathy, K. S. Narayanan, and L. Arockiam, "Study on kinetic parameters of different biomass samples using thermo-gravimetric analysis," *Biomass and Bioenergy*, vol. 58, pp. 58-66, 2013.

[12] J. E. White, W. J. Catallo, and B. L. Legendre, "Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies," *Journal of Analytical and Applied Pyrolysis*, vol. 91, pp. 1-33, 2011.

[13] F. Yao, Q. Wu, Y. Lei, W. Guo, and Y. Xu, "Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis," *Polymer Degradation and Stability*, vol. 93, pp. 90-98, 1// 2008.

[14] M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, and R. Dewil, "Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction," *Renewable Energy*, vol. 35, pp. 232-242, 1// 2010.

[15] K. P. Shadangi and K. Mohanty, "Kinetic study and thermal analysis of the pyrolysis of non-edible oilseed powders by thermogravimetric and differential scanning calorimetric analysis," *Renewable Energy*, vol. 63, pp. 337-344, Mar 2014.

[16] K. Bousdira, " Potentiel énergétique de la biomasse phoenicicole en Algérie - évaluation et recommandation.," presented at the IVème Congrès International sur les Energies Renouvelables et l'Environnement Tunisie, Monastir, 2009.

[17] J.-L. DAUDON, "Thermogravimétrie," *Techniques de l'ingénieur*, vol. p1260, pp. P 1 260: 2-21, 2014.

[18] M. S. Duvvuri MS, Iqbal KZ, Welker JR., "The pyrolysis of natural fuels," *Journal of Fire and Flammability* vol. 6, p. 468±77, 1975.

[19] K. G. Mansaray and A. E. Ghaly, "Physical and thermochemical properties of rice husk," *Energy Sources*, vol. 19, pp. 989-1004, Nov 1997.

[20] J. Guo and A. C. Lua, "Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction model," *Biomass and Bioenergy*, vol. 20, pp. 223-233, 3// 2001.

[21] A. Kumar, L. Wang, Y. A. Dzenis, D. D. Jones, and M. A. Hanna, "Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock," *Biomass and Bioenergy*, vol. 32, pp. 460-467, 2008.

[22] S. V. Vassilev, D. Baxter, and C. G. Vassileva, "An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types," *Fuel*, vol. 117, pp. 152-183, 2014.

[23] G. M. Friedman, "Identification of Carbonate Minerals by Staining Methods," *Journal of Sedimentary Petrology*, vol. Vol. 29 pp. 87-97, 1959.

[24] F.-X. Collard and J. Blin, "A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin," *Renewable and Sustainable Energy Reviews*, vol. 38, pp. 594-608, 2014.

[25] N. Saadaoui, A. Rouilly, K. Fares, and L. Rigal, "Characterization of date palm lignocellulosic by-products and self-bonded composite materials obtained thereof," *Materials & Design*, vol. 50, pp. 302-308, 2013.

[26] W. H. Barreveld, "Date palm products," *FAO AGRICULTURAL SERVICES* vol. BULLETIN No. 101, 1993.