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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Combustion Study of Phoenicicole Biomass in Algerian Oasis Using Thermogravimetric Analysis: Deglet Nour Cultivar Case

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Abstract The importance of date palm (*Phoenix dactylifera* L.) deposit could represent an interesting solution for sustainable and integrated energy valorization in Algerian oasis ecosystem. The objective of this work is to study the thermal behavior, under an oxidative atmosphere of the phoenicicole biomass main constituents related to the dominant cultivar, Deglet Nour. Thermogravimetric analysis is the approach used to study the pyrolysis behavior of this lignocellulosic biomass by the determination of the kinetic constant (activation energy, order of the reaction, pre-exponential factor) and the description of different thermal profiles. The results show that combustion process could be an interesting alternative energy recovery for the phoenicicole biomass. This is explained by the low activation energy which is estimated at an average of 29.06 k J/mol and the low residues generated by the thermoconversion. Furthermore, two types of phoenicicole waste have been identified by their combustion behavior: firstly the lif part characterized by their thermal stability due to the high lignin content and secondly the fruit bunch (ARJ) characterized by a great thermal reactivity.

Keywords Date palm biomass · Thermogravimetric · Kinetics · Combustion · PCA

Abbreviations

%	Percent
ΔMass	Combustion yield (%)
°C	Degree Celsius
A	Ash concentration (%)
AD	Rachis
A_f	Pre-exponential factor (s^{-1})
ANOVA	Analysis of variance
ARJ	Fruit bunch
C	Carbon mass fraction (%)
CF	Fixed carbon
DJ	Palm
DN	Deglet Nour cultivar
DTA	Differential thermal analysis
DTG	Temperature derivative of the mass loss
E	Activation energy (kJ/mol)
GH	GHARS cultivar
HHV	Higher heating value (gross calorific value)
MJ/kg	Mega joule per kilogram
n	Order of reaction
PCA	Principal component analysis
R	Universal gas constant (8.314 J/mol K)
R^2	Regression coefficient
S	Sulphur mass fraction %
SA	Fruit stalk pruning
T	Temperature (K)
t	Time (s)
TGA	Thermogravimetric analysis
T_i	Ignition temperatures of combustion (°C)
T_b	Burnout temperatures of combustion (°C)

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URAER	Unit of applied research in renewable energies Ghardaïa
VM	Volatile matter (%)
w	Mass of the sample at a particular time t

1 Introduction

The negative consequences of the production and the use of fossil fuels have caused a global craze for renewable energy. Biomass is a sustainable alternative that could address this issue. It has many advantages that make it competitive and complementary to other renewable energies: substantially contribution to the CO_2 emission reduction targets defined in the Kyoto protocol, a substantial deposit (especially lignocellulosic resources) and a waste recycling [1–3]. In the oasis ecosystem, despite the aridity of the environment, the date palm tree (*Phoenix dactylifera* L.), thanks to its many assets (biochemical, ecological, socioeconomic, environmental) [4–11], could be considered an attractive and sustainable energy source. The thermal behavior study of this biomass is an essential step for an initial evaluation of its energy quality [8,12,13].

There are various energy conversion processes (biological and thermochemical), from lignocellulosic biomass. Several parameters interact with the selection of possible combinations among raw materials—processes—products, but not all are possible from a practical point of view. Combustion proves to be simple, attractive, and practical for this type of resource. Let it be recalled that the combustion is defined as a complex sequence of exothermic chemical reactions between a fuel and an oxidant, accompanied by the production of heat and sometimes associated with light in flame form. The basic stoichiometric equation for the combustion of wood, represented by the empirical formula of cellulose, ($C_6H_50_5$), is illustrated by Eq. 1 [1,3]:

$$(C_6H_{10}0_5)n + 6nO_2 \quad \rightarrow 6nCO_2 + 5nH_20 \tag{1}$$

The characterization of this recovery process (kinetic study and thermal profile), namely the biomass combustion, is done by various analytical techniques: thermogravimetric analysis (TGA), differential thermogravimetry (DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA) [2,12]. A literature review shows that the TGA is the simplest technique and the most commonly used for observing the combustion of a fuel in general and a biomass in particular [12]. This technique is based on the determination of the weight change depending on the temperature and that essentially considers the weight, temperature and time. It takes in consideration the Arrhenius model applied to derivative thermogravimetric (DTG) for determining parameters responsible for the prediction of the biomass thermal behavior [10,12,14–16].

The resource studied in this article is the phoenicicole biomass with its various constituents. This choice is based on a series of arguments. The first is the scarcity of studies on the energy aspect of this resource in general and on varietal aspect in particular [7,8]. Only three studies were cited in the bibliography: Bousdira et al. [7,8] took into consideration all the phoenicicole biomass constituents of an Algerian cultivar (namely Ghars). Sait et al. [10] and Elmay et al. [9,17] studies focused, respectively, on five and three residues of date palm biomass, ignoring the varietal aspect. The second argument involves the importance of phoenicicole deposit in the Algerian oasis (having reached 807,992 tons in 2012) and its chemical ability to energy recovery. This is precisely the case of the Algerian famous cultivar, namely Deglet Nour, chosen for our article whose local and national importance has been proven (40% of Algerian phoenicicole park); in addition, this cultivar generates significant quantities of residue (65 kg/tree/year). Finally, the optimization use of this abundant and available biomass is the last argument that motivates its choice for this study [5–8,18].

In summary, this work aims to study the phoenicicole biomass (DN cultivar case) under combustion process (10 °C/min) using thermogravimetric analysis (TGA) [19]. TGA data have been treated by two statistical analysis, i.e., analysis of variance (ANOVA) and principal component analysis (PCA). 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 combustion process? What are their kinetic (activation energy, order of the reaction, pre-exponential factor) and the thermal characteristics? What are the most interesting phoenicicole biomass constituents, related to DN cultivar, for combustion process?

The area chosen for the realization of this study is the Guerrara oasis (Algeria—32° 47′ north longitude: 4° 30′ east latitude), which served as a model for the study of biomass deposit at the regional (Mzab) and national level (Algerian oasis) [5,7,18].

2 Materials and Methods

2.1 Methods of Sample Preparation and Chemical Composition

Sampling, sample preparation and analysis (proximate, ultimate and calorimetry) were conducted according to the standards described in [7] .

Table 1 Specifications and test condition of thermogravimetric analyzer font

Model balance sensitivity	Setsys Evolution 16/18 (model with integrated controller CS32)
Balance accuracy	0.4 µg
Maximum weight	200 mg
Temperature range	25–1600 °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 N_2, Ar, CO_2, air, O_2 or other inert or active gases
Temperature sensors	S-type thermocouple with 10% rhodium platinum
Heating rate	10 °C/min
Purge gas	20% O_2 + 80% He
Purge gas rate	200 ml/min
Initial temperature	25.00 °C
Final temperature	700 °C

2.2 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 1.

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 [20]. 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 [10,16,21–26] that used for our case is based on the Shadangri et al. method [16]. All these kinetic models are based on the Arrhenius equation given by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A_{\mathrm{f}} \cdot e^{-\left(\frac{E}{RT}\right)} \cdot (1-\alpha)^n \tag{2}$$

where $\mathrm{d}\alpha/\mathrm{d}t$, A_{f}, 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 :

$$\alpha = \frac{w_0 - w}{w_0 - w_{\mathrm{f}}} \tag{3}$$

- The constant heating rate β is given by:

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{4}$$

where w, w_0 and w_{f} are, respectively, the weight of the sample at a particular time t, its initial and final weight. Equation (1) is written:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A_{\mathrm{f}}}{\beta} \cdot e^{-\left(\frac{E}{RT}\right)} \cdot (1-\alpha)^n \tag{5}$$

$$\frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \frac{A_f}{\beta} \cdot e^{-\left(\frac{E}{RT}\right)} \cdot \mathrm{d}T \tag{6}$$

Taking into account the considerations [16]:

- Rearrangement and integration of Eq. (6)
- Approximation of the order of the reaction to the unity

Equation (5) becomes:

$$-\mathrm{Ln}\,(1-\alpha) = \frac{A_f}{\beta} \cdot \frac{RT^2}{E} \cdot e^{-\left(\frac{E}{RT}\right)} \tag{7}$$

$$\mathrm{Ln}\,(-\mathrm{Ln}\,(1-\alpha)) = \mathrm{Ln}\frac{A_f}{\beta} \cdot \frac{RT^2}{E} - \frac{E}{RT} \tag{8}$$

This equation is of the form:

$$\boldsymbol{y} = \boldsymbol{b} + \boldsymbol{a} \cdot \boldsymbol{x} \tag{9}$$

where

$$\boldsymbol{y} = \mathrm{Ln}\,(-\mathrm{Ln}\,(1-\alpha))\,; \quad \boldsymbol{b} = \mathrm{Ln}\frac{A_f}{\beta} \cdot \frac{RT^2}{E}; \quad \boldsymbol{x} = \frac{1}{T}$$

The constant $a = -\frac{E}{R}$ 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 3.

2.3 Statistical Treatment Parameters

The statistical approach used for the examination of TGA data is the analysis of variance (ANOVA) and the principal component analysis (PCA) applied to thermal, kinetics and chemical parameters.

Table 2 Chemical composition of date palm constituents—DN case (see type of font)

Phoenicicole biomass	Proximate composition				Ultimate composition				HHV
	M	VM	A	FC	C	H	O	N	
	%	%	%	%	%	%	%	%	MJ/kg
Rachis (AD)	5.86	68.47	6.19	25.32	43.02	5.75	41.76	0.00	17.86
Fruit bunch (ARJ)	6.13	66.59	8.02	25.30	44.32	5.72	39.53	0.40	20.44
Palm (DJ)	6.42	62.98	18.79	18.11	41.15	5.56	34.06	0.18	19.82
Petiole (KER)	8.91	60.37	10.62	28.05	41.02	4.93	38.64	0.00	19.26
Spathe (KH)	7.38	66.75	6.60	26.20	44.29	5.32	40.60	0.81	19.58
Lif (LIF)	7.33	52.35	20.15	27.05	27.61	3.46	30.63	0.35	15.34
Fruit stalk pruning (SA)	5.14	68.83	7.47	23.91	43.58	5.28	39.47	0.31	19.20
Mean	6.74	63.76	11.12	24.85	40.71	5.15	37.81	0.29	18.79
Min.	5.14	52.35	6.19	18.11	44.32	5.75	41.76	0.81	15.34
Max.	8.91	68.83	20.15	28.05	27.61	3.46	30.63	0.00	20.44

The thermal parameters include: ignition and burnout temperatures of combustion, the corresponding activation energies and the yield of the thermochemical process and the calorific value of biomass (HHV). However, chemical parameters correspond to proximate parameters (fixed carbon FC, volatile matter VM and ashes A). The moisture parameter was not taken into account for the PCA because of its low variability.

3 Results and Discussion

3.1 Chemical Composition

Chemical characterization of the studied phoenicicole biomass, performed in the previous study [7], is illustrated in Table 2. It revealed the compatibility of the studied biomass with conventional solid biofuels. Indeed, the proximate analyzes have shown the low concentration of moisture and the variability of ash concentration between the by-products (5 and 12%). The energetic aspect of the studied phoenicicole biomass indicates the appreciable calorific value of all samples (17 MJ/kg), excepted fibrilium part which presents lower values (15 MJ/kg). The elementary composition CHO shows a big compatibility of the studied biomass with conventional biofuels mainly agricultural waste and wood. The analysis of S and N contents shows a low values (<0.2 and $<0.4\%$, respectively) which presents a very advantageous characteristic for the studied biomass.

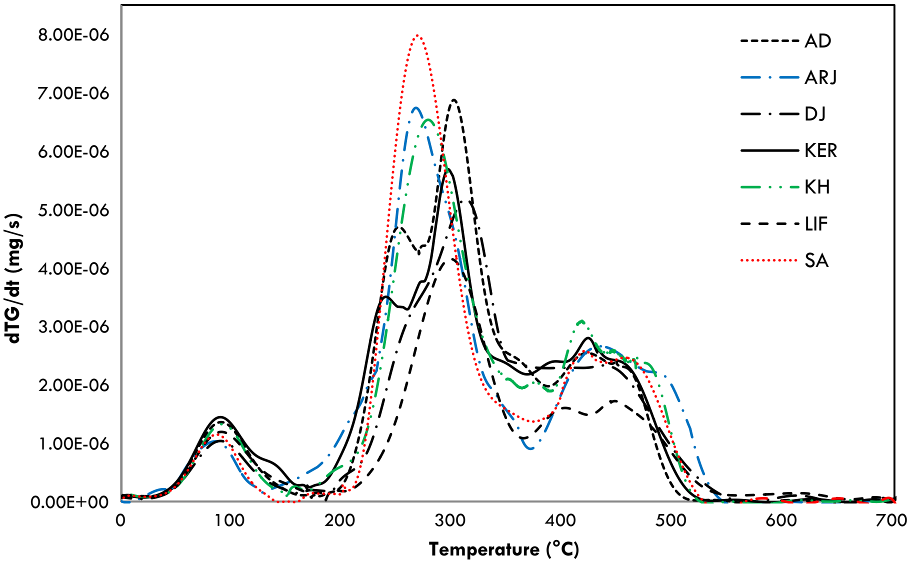
3.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the phoenicicole main residues (DN cultivar case) carried out under an oxidative atmosphere at 10 °C/min (Fig. 1) represents derivatives mass (dTG) depending on the temperature. This figure shows the principal combustion phases of phoenicicole biomass:

- The first stage corresponds to the initial weight loss which is due to evaporation of moisture. It begins at ambient temperature and ends at approximately 165 °C. It can reach 185 °C.
- This phase is followed by a major weight loss (200 °C–400 °C) which is due to the devolatilization of biomass and the oxidation of the char. In this extended temperature range, important thermal degradation of biomass has been observed. This phase is also associated with a release of gas, mainly CO_2 and CH_4.
- The final phase is characterized by a loss of nonsignificant weight in the temperature range between 375 and 700 °C. This weight reduction is due to the oxidation of carbon residues in inorganic solids [27]. Between 450 and 600 °C, there is the release of chemically bound CO_2 and water vapor formed chemically. For temperatures above 538 °C (which can start from 345 °C in some cases), almost no weight loss was observed. The final process (600–700 °C) involves the evolution of carbon containing compounds such as carbon oxides, tars and hydrocarbon gases (heavy hydrocarbons such as fluorene, phenanthrene, the fluoranthene, and benzo (a) pyrene). The oxidation of Char continues until all the carbon is oxidized [27,28].

The overlap of certain changes during the three phases (devolatilization of volatiles matter, combustion and char transformation), especially for temperatures <600 °C, makes their delimitation process difficult. Thus, a series of actions have been made to minimize this overlap, namely the reduction in the sample size and the decrease in the heating rate (10 °C/min) [10,27,28].

Fig. 1 Typical dTG diagrams of the phoenicicole biomass related to the DN cultivar under oxidative atmosphere



The difference in the phoenicicole biomass composition (lignin, hemicellulose, cellulose) especially on mineral level [7,29,30] caused the variation of the thermal behavior (profile) between biomass components (see Fig. 1).

3.3 Kinetic Parameters

The calculation of the kinetic parameters has taken in consideration temperature interval where the thermal decomposition process is the most important (maximum degradation rate).

This procedure has facilitated the interpretation of the charts and has allowed reaching significant correlation coefficients R^2 (Fig. 2; Table 3). Indeed, for combustion process, this rate varies between 0.94 and 0.98 (an average of 0.97).

Table 3 and Fig. 3 show the combustion kinetic parameters (activation energy, reaction order and pre-exponential factor) of the phoenicicoles main residues related to Deglet Nour cultivar in the Guerrara oasis. It should be recalled that the activation energy is the energy that a collision has to bring forth to the reagents for triggering a reaction. In other words, for thermal processes applied to our biomass, this entity is the energy necessary for triggering of the thermal conversion [31].

Considering combustion process for the phoenicicole biomass studied (Table 3; Fig. 3), the activation energy is estimated on average to 28.69 kJ/mol (KER) and varies between 25.32 kJ/mol (LIF) and 30.77 kJ/mol (KH). Despite the complexity and heterogeneity of reactions involved in combustion compared with pyrolysis [32], the presence of oxygen seems to have no effect on the thermal behavior from the studied phoenicicole biomass independently of its chemical composition. This means it needs to almost the same energy for the combustion of each date palm biomass. From a previous study [8,13], the pyrolysis activation energy from phoenicicole biomass corresponding to the same cultivar (DN) is estimated to average 28.78 kJ/mol. Thus, regarding the case of the DN variety, the analysis of variance shows that there are no difference ($P = 78.08\% > 5\%$) between the energy involved for thermal degradation under inert and oxidative atmosphere (see Table 4).

The order of the reaction (n) is estimated to be about 0.56 (KER) on average for the whole studied by-products. It varies between 0.26 (ARJ) and 1.57 (KH). The values of n which tend to zero (case of SA and ARJ) correspond to slow reactions where there is a passive combustion. For the rest, burning could be considered as active (fast reaction) [19].

The pre-exponential factor varies significantly between 4.30 and 14.30 s^{-1} for the combustion process.

3.4 Classification of the Main Phoenicicole Biomass

Principal component analysis applied to chemical parameters and thermal variables related to the combustion process provides a classification of the studied biomass. Four categories were identified (Fig. 4; Tables 5, 6):

The **first group** includes the Lif part which is characterized by a high ignition and burnout temperatures (185–540 °C). Its low combustion rate (62%) is due to the high lignin content.

The **second group** corresponds to the inflorescence part (fruit stalk pruning (SA), fruit bunch (ARJ) and spathe (KH)). Unlike the previous group, this category is characterized by low ignition temperature (126 °C) but a higher combustion rate (approx. 93%) and high calorific value (20 MJ/kg). This is mainly due to the predominance of hemicellulose (54%) which is very unstable thermally.

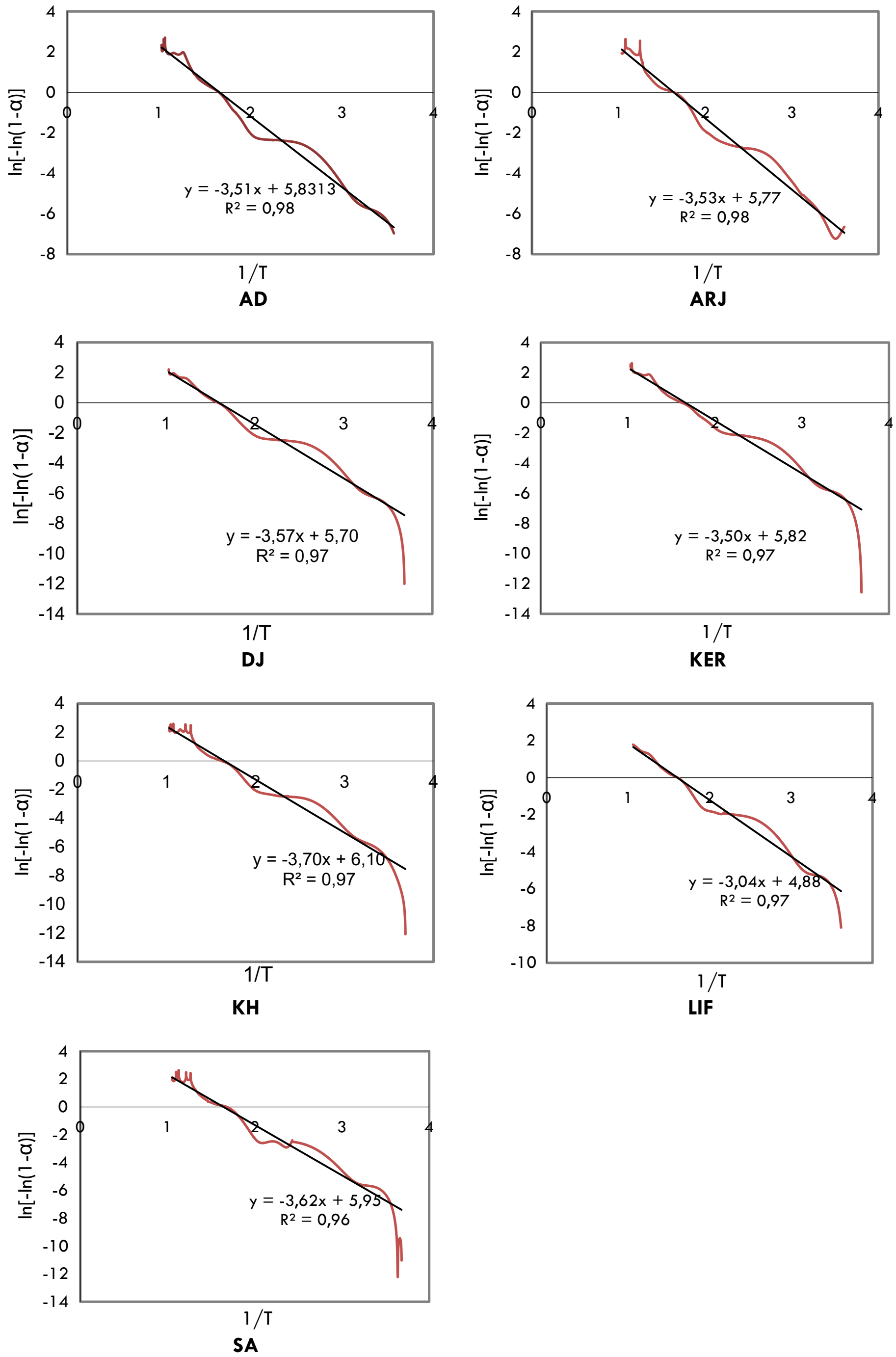


Fig. 2 Kinetic plots for the DN phoenicicole biomass under oxidative atmosphere at 10 °C/min

The **third group** composed of the palm (DJ). It is characterized by high burnout temperature (557 °C) and a high gap between the beginning and the end of the depolymerization of hemicellulose and cellulose which are in equivalent proportion (29.70 and 23.30%, respectively). Chemical composition of this group is characterized by a low fixed carbon estimated at 19.24% and a high ash content (∼15.36%) which could have a catalytic effect on the combustion process that explains the high heating value (∼19.38 MJ/kg).

The **fourth group** is represented by the basal part of the palms, i.e., the petiole (KER) and the rachis (AD). It is characterized by intermediate devolatilization temperatures and mean combustion rate due to equivalent concentrations of cellulose and hemicellulose.

Table 3 Kinetic parameters of phoenicicole biomass (DN cultivar case) under oxidative atmosphere (IDEM)

Biomass	Linear regression		Regression coefficient	Activation energy	Pre-exponential factor	Reaction order
	b	a	R^2	E (kJ/mol)	$B = \ln(A)$	n
AD	−3.51	5.83	0.98	29.15	1.70	0.44
ARJ	−3.53	5.77	0.98	29.31	2.02	0.26
DJ	−3.57	5.70	0.97	29.65	2.41	0.55
KER	−3.50	5.83	0.97	29.12	2.29	0.56
KH	−3.70	6.10	0.97	30.77	2.66	1.57
LIF	−3.04	4.88	0.97	25.32	1.46	0.80
SA	−3.62	5.95	0.96	30.09	2.51	0.28

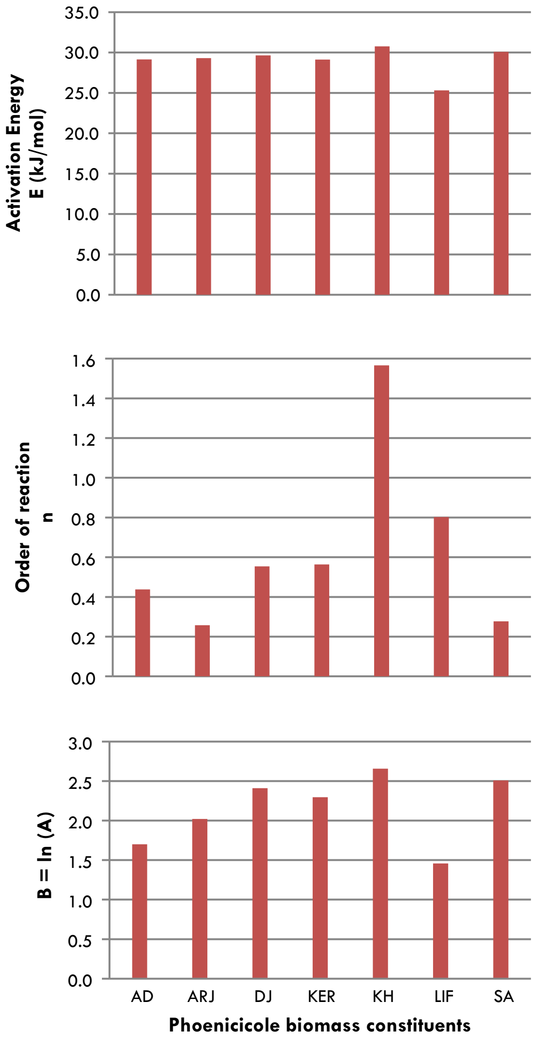


Fig. 3 Kinetic parameters of phoenicicole biomass (DN cultivar case) under oxidative atmosphere at 10 °C/min

3.5 Correlation Between Proximate Composition Immediate and Thermal Parameters

The main correlation among the thermal parameters and the immediate composition is illustrated in Table 7.

Table 4 Analysis of variance (ANOVA) of activation energy related to phoenicole biomass (DN and GH cultivars) under inert [8, 13] and oxidative atmosphere (IDEM)

Source of variations	Sum of squares	Degrees of freedom	Mean square	F[a]	P value (%)
Between groups	0.29	1	0.29	0.08	78.08%
Within groups	43.39	12	3.62		
Total	43.68	13			

[a] Test of Fischer

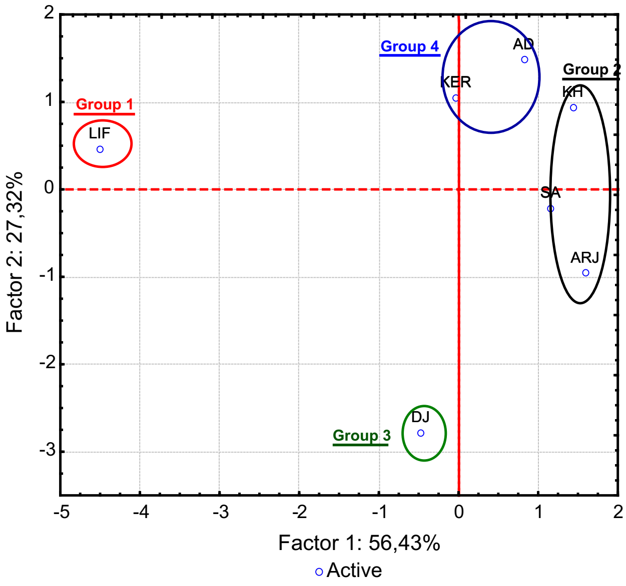


Fig. 4 Projection of phoenicicole biomass (individuals) on the factor-plan (1 × 2) (DN cultivar case) under oxidative atmosphere at 10 °C/min

The positive correlation (+0.79) between the activation energy of the combustion and the calorific value is explained by the principle of energy conservation [33]. Indeed, a high energy involved in triggering a combustion reaction (corresponding to E) generates (releases) obligatorily an amount of high energy recovered after complete combustion (corresponding to HHV) and vice versa.

Table 5 Classification of phoenicicole biomass by PCA

Phoenicicole biomass constituents		T_i (°C)	T_b (°C)	ΔCOM (%)	E (kJ/mol)	CEL (%)	HEM(%)	LIG (%)	VM(%)	A (%)	FC (%)	HHV (MJ/kg)
GR1	LIF	185.32	539.73	62.54	25.31	50.60	8.10	31.90	52.35	20.15	27.05	15.34
GR2	ARJ, KH, SA	155.94	536.71	93.07	30.06	29.67	48.87	14.47	67.39	7.36	25.14	19.74
GR3	DJ	171.30	556.92	81.99	29.65	29.70	23.30	11.60	62.98	18.79	18.11	19.82
GR4	AD, KER	173.32	521.33	91.90	29.14	36.90	30.15	16.10	64.42	8.40	26.68	18.56
	MAX.	185.32	556.92	94.08	30.77	50.60	54.50	31.90	68.83	20.15	28.05	20.44
	MIN.	125.93	516.43	62.54	25.32	26.00	8.10	11.60	52.35	6.19	18.11	15.34
	MOY	167.30	535.63	86.79	29.06	34.73	34.04	17.01	63.76	11.12	24.85	18.79

Table 6 Main combustion phases for phoenicicole biomass groups

	Group 1	Group 2	Group 3	Group 4
	LIF	SA, ARJ, KH	DJ	KER, AD
Hemicellulose and cellulose degradation	$T = [185–365]$ °C	$T = [126–376]$ °C	$T = [171–350]$ °C	$T = [173–358]$ °C
	Max. weight loss ~298°C	Max. weight loss ~ 270 °C	Max. weight loss ~ 311 °C	Max. weight loss ~ 300 °C
	Reactions : A small decomposition interval of the two major constituents, explained by a high hemicellulose content (54%), which in the presence of a high proportion of minerals (LIF) behaves like lignin in particular during the carbonization phase ($T > 300$ °C where the benzene compounds obtained from this transformation are assimilated to the constituents of lignin [35,38].)	Reactions: Wide decomposition interval of the two major constituents due to the high content of hemicellulose whose maximum mass loss is about of 270 °C	Reactions: Significant overlap in the devolatilization process of lignin due to its low concentration (11.60%)	Reactions: Slight shoulder between 250 °C and 269 °C attributed to maximum mass loss of hemicellulose. Pronounced shoulder, observed between 295 °C and 300 °C, attributed to the maximum devolatilization rate of cellulose. Undeniable overlap in the lignin devolatilization could occur during this phase
Lignin degradation	$T = [340–540]$ °C	$T = [126–546]$ °C	$T = [350-549]$°C	$T = [358-526]$ °C
	Max. Weight loss ~ 442°C	Max. Weight loss ~[406−431]°C	Max. Weight loss ~ 453°C	Max. Weight loss ~ 421°C
Char oxidation	$T > 540$ °C	$T > 523$ °C	$T > 549$ °C	$T > 526$ °C
	Residues: 27.83%	Residues: 5.72–13.73%	Residues: 13.65–18.01%	Residues: 6.43–10.99%

The positive correlation (+0.61) between the combustion rate and the volatile matter is explained by the fact that these two entities are closely linked. Indeed, the first one includes the second to which is added the moisture content and a proportion of fixed carbon. Let it be recalled that the volatile matter of a biofuel corresponds to its loss of mass by eliminating moisture when the solid biofuel is heated under standard conditions without contact with air [34], while the combustion rate under TGA corresponds also to the weight loss without prior removal of moisture and in the presence of air. In this particular case, the ash essentially constitutes the residual mass. This explains the negative correlation (−0.77) between the latter and the combustion rate. This leads us to conclude that the last correlation constitutes an arithmetic consequence of the relation ($A = 100 - \text{MV} - \text{CF}$).

Table 7 Correlation matrix of proximate composition and combustion thermal parameters

	T_{i}	T_{b}	ΔCOM	E	VM	A	FC	HHV
T_{i}	1.00							
T_{b}	−0.05	1.00						
ΔCOM	−0.39	−0.05	1.00					
E	−0.36	0.17	**0.88**	1.00				
VM	−0.34	0.10	**0.85**	**0.68**	1.00			
A	0.48	0.32	**−0.77**	**−0.54**	**−0.75**	1.00		
FC	−0.17	**−0.58**	−0.19	−0.26	−0.42	−0.28	1.00	
HHV	−0.40	0.40	**0.69**	**0.79**	0.49	−0.23	−0.43	1.00

Bold values indicate the significant correlations of proximate composition and combustion thermal parameters

The positive correlation (+0.88) between the combustion activation energy and the combustion rate means that high ignition energy generates a high rate of transformation of the biomass via this process and vice versa. The first case characterized by $E \sim 30$ kJ/mol, ΔCOM ∼ 91% (high) and A ∼ 7% (low), corresponds to the inflorescence part (spathe and fruit bunch) where hemicellulose constitutes the major element (54%). This compound, due to its biochemical composition, has a high carbonization efficiency attributed to the catalytic effect of minerals [35,36]. The lif case is characterized by E ∼ 26 kJ/mol, ΔCOM ∼ 67% (low), a high ash content A ∼ 20% and especially a high proportion of lignin; we have an inverse situation translated by a low activation energy and a low combustion rate. Thus, the combustion efficiency of the latter compound is low, due to its thermal stability. The negative correlation between E and A is explained by what has been said above, as well as the inverse relation between the combustion efficiency and the ash rate.

The positive correlation (+0.69) between the calorific value and the combustion efficiency is explained by the principle and the definition of the calorific value fixed by the solid biofuels standards. These standards define this entity as "the absolute value of the specific combustion energy in joules released per unit mass of solid biofuel burned in oxygen in a calorimetric bomb under specified conditions" [37].

4 Conclusions

Thermogravimetric analysis (TGA) was performed to study thermal behavior under oxidative atmosphere of the phoenicicole main constituents related to Deglet Nour cultivar. The approach used is based on the calculation of the kinetic parameters (activation energy reaction order and pre-exponential factor) and the review of the different thermal characteristics related to the biomass decomposition phases.

The thermal profile of the phoenicicole biomass is characterized by three decomposition stages corresponding to: dehydration, devolatilization of biomass and the combustion and the oxidation of carbon residues in inorganic solids.

The analysis of kinetic parameters especially activation energy shows that there is no variation among different lignocellulosic phoenicicole biomass (corresponding to Deglet Nour cultivar) considering oxidative (combustion) and inert (pyrolysis) thermoconversion.

The principal component analysis applied to combustion parameters of DN phoenicicoles biomass has attended almost the same classification obtained previously for pyrolysis process. Four groups have been identified for the two thermochemical processes. The common and atypical category consists of LIF part, which is characterized by a low calorific value and thermal stability due to the high content of lignin. In contrast to the previous category, the inflorescence knows an opposite trend, namely a high thermal reactivity and an interesting calorific value, which promotes the biomass for a possible energy recovery. The remaining two groups have the intermediate parameters.

Finally, the combustion of the biomass appears to be more advantageous than pyrolysis because it generates smaller amounts of residue.

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