

## An overview of the chemical composition of phoenicicole biomass fuel in Guerrara oasis

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**Abstract** - This study aims at the chemical characterization of the phoenicicole biomass for the conversion of the main by-products related to the date palm (*Phoenix dactylifera* L.). Experimental study led to the conducting of immediate analysis (moisture, ash, volatile matter and fixed carbon), the evaluation of calorific value and the determination of elemental analyzes by calculations based on empirical model set on volatile matter and ash. An analysis of the links between these parameters was also conducted. The results of our study showed that the moisture concentration is less than 5 % and the ash concentration is very variable between 4.7 and 11 %, the experimental calorific value of the phoenicicole biomass is estimated at an average of 17.56 MJ/kg, finally the calculation of the error between the experimental HHV and the HHV calculated is around 3 %. The calculated elemental composition showed a big compatibility of the studied biomass with conventional biofuels mainly agricultural waste and wood. A summary of these results revealed an inverse relationship between the calorific value and ash and moisture concentration, as well as the significant impact of the ash concentration on the energy value of the biomass compared to the moisture concentration and the elemental composition.

**Keywords:** Phoenicicole Biomass - Chemical composition - Higher heating value - Proximate composition - Ultimate composition.

### 1. INTRODUCTION

Energy plays a central role in the global economy. Algeria has an important energy field, it ranks third among the oil producing countries in Africa and the 12<sup>th</sup> largest producer in the world [1].

Despite the importance of this position, according to a detailed report prepared by experts of the Organization of the Petroleum Exporting Countries OPEC, Algerian oil field may know a drop in reserves and production. This is due, among other things, to the increasing national energy consumption. Indeed, the Minister of Energy and Mines said that it has increased by 15% per year [2]. Moreover, the exploitation of this fossil energy is sometimes inaccessible, expensive and polluting (greenhouse gas emissions), particularly in arid and semi-arid areas [3].

Thus, the search for clean alternative energy becomes an emergency for sustainable development in these areas. Biomass can be an interesting partial energetic solution if it's about a local and available field. The phoenicicole biomass meets these two requirements. Indeed, the study of Bousdira (2010) [4, 5] showed a significant energy potential generated by the main by-products of the date palm in M'zab area and at the national scale as well. These studies show that in the national scale (Algeria), the quantity of phoenicicole lignocellulosic waste is about 673,438 tons; that is to say phoenicicole energy is about 268,616 tons of oil equivalent.

Energy conversion cannot be considered without a deep knowledge of the physical, chemical and energetic composition of these resources.

This study is a part of the research project 'Assessment of energy biomass resource in arid and semi-arid areas' conducted by the research team 'Renewable Energy Resources' of the Applied Research Unit in Renewable Energies URAER / Ghardaïa. It aims at the energetic characterization of the main by-products of the date palm (*Phoenix dactylifera* L) related to Deglet Nour and Ghars cultivars, and is based on conducting immediate analyzes (moisture, ash, volatile matter and fixed carbon), the evaluation of calorific value as well as the determination of elemental analysis by calculation based on empirical model related to volatile matter and ash concentration. The determination of these parameters allows the prevention of the considered biomass energy behavior and the choice of the adequate conversions.

### 2. MATERIAL AND METHODS

#### 2.1 Presentation of samples and the study area

The samples studied represent the palm tree by-products (**Table 1**) taken from the two most dominant cultivars (Deglet Nour and Ghars) in the oasis of Guerrara - Algeria (Latitude: 32° 47' North Longitude: 4° 30' East) (Fig. 1).

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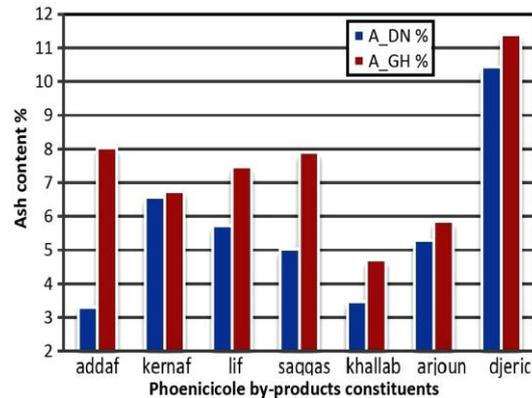


Fig. 2: Ash concentration of cultivars GH and DN by-products in Guerrara oasis

This parameter is highly variable and depends on several factors including the growing conditions of the plant, the geographical location, the radiation, the composition of water for irrigation, fertilization, soil quality and the variety of the plant [16, 17].

The high concentration of ash in the *djerid* part is explained by the fact that the foliage of the tree which is the main focus of photosynthetic metabolism [18].

The *khallab* part, protection organ of floral scape, presented as a bract of ligneous structure [19], shows the content the lowest ash.

This parameter is an important energetic criterion mainly for combustion. Indeed, the ash is formed from two components with negative effects for this conversion: home ash (forming slag) and flying ash (generating acid smokes) [20].

Nevertheless, at well-defined proportions, some minerals can catalyze the combustion. This is particularly the case of:

- $K^+$  or  $Ca^{2+}$  promote the cycle opening and creation of light carbonyl mixtures (pyrolysis stage of the combustion process ) [21]
- Alkaline earth chlorides (eg.  $MgCl_2$ ) with water vapor leading to the development of HCl for thermal degradation of cellulose:  $MgCl_2 + 2 H_2O \rightarrow Mg(OH)_2 + 2 HCl$  ( $T \approx 250-300^\circ C$ ) [22]. The production of HCl stimulates the acid-catalyzed degradation of biomass and catalyzing the dehydration prior to thermal degradation causing a cross linking of the cellulose chains track.

The average ash concentration of the whole studied biomass (~ 6.5 % DM) compared with the biomass used as biofuel is above its concentration in wood (3.5 %), and agricultural biomass (5.7 %). The trend is largely reversed in comparison with the animal biomass (30.9 %), micro algae (23.6 %) and coal (20.9 %). This setting is quite comparable to the mixture of agricultural and forest residues (7.7 %) (olivecake , wheat and corn straws, grape pomace) and pine bark (6 %) [16].

The relatively high concentration of this parameter can be corrected by pre-treatments of the biomass and a series of other measures to mitigate the problems associated with inorganic compounds [23, 24]:

- Reducing combustion temperature.
- Water cooling at the combustion area.
- Adding an additive such as quicklime (1-2%) during storage to increase the ash melting point.
- Use of fuels with minimal silica.
- Regular agitation of ashes.

### 3.2 Moisture concentration of cultivars GH and DN by-products in Guerrara oasis

A general observation of the moisture concentration of the main waste from cultivars DN and GH in Guerrara oasis, as shown in Figure 3, shows not a very significant variation of this parameter between the different wastes and varieties:

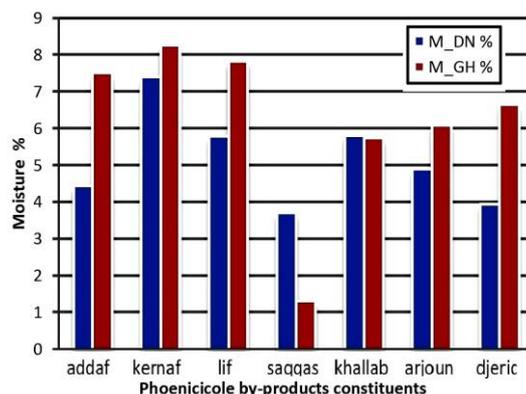


Fig. 3: Moisture concentration of cultivars GH and DN by-products in Guerrara oasis

- Moisture rate of DN cultivar by-products rate ranges from 3.71 % (*saqqas* case) to 7.40 % (*kernaf* case). The average value is estimated at 5.14 % (*arjoun* case).
- As regards GH cultivar, moisture varies between 1.30 % (*saqqas* case) and 8.26 % (*kernaf* case). It is estimated on average at 6.13 % (*arjoun* case).
- The average moisture of GH variety (6.13 %) is higher than DN cultivar (5.14 %).
- Moisture from most cultivar GH by-products is higher than DN except *saqqas*\_GH (1.30 %), it is smaller than DN (3.71 %). Moreover, *khallab* moisture of the two varieties is almost equivalent.

The preceding observations indicate that *saqqas* is the lowest wet by-product, this can be explained by its high concentration of cellulose (36.55 %) compared with *kernaf* (30.7 %) [25], which gives it a rigid appearance unlike the latter which has a very 'porous' appearance.

Considering the phenicole biomass studied entirely (by-products), the standard of moisture concentration is very interesting (~ 5%) and has many advantages for storage and thermal conversion (combustion, pyrolysis or gasification) without pre-treatment (through natural drying of the biomass). Indeed, a high moisture concentration would slow thermal processes and damage their quality [23].

This parameter knows another trend for biomass used as biofuel: Wood (19.3%), agricultural biomass (12.7%), animal biomass (30.9%), micro algae (10.7%), a mixture of agricultural and forest residues (17.3 %) [24]. This makes the palm tree by-products the preferred choice by considering this criterion only for thermal energy conversion.

### 3.3 Higher heating value of cultivars GH and DN by-products in Guerrara oasis

A general observation of the calorific value (heating value) of the main wastes related to cultivars DN and GH in Guerrara oasis, shown in Figure 4, shows not a significant variation of this parameter between the different wastes:

- The calorific value of cultivar DN by-products varies between 17.2 MJ/kg (*addaf* case) and 18.3 MJ/kg (*khallab* case). The average value is estimated at 17.8 MJ/kg (case of *kernaf*).
- For GH cultivar, the calorific value of the by-products ranges between 16.9 MJ/kg (*kernaf* case) and 18.4 MJ/kg (*djerid* case). It is estimated at an average of 17.6 MJ/kg (*arjoun* case).
- The calorific value of DN cultivar by-products is higher than those of GH by-products, except *khallab* and *djerid* which are experiencing an opposite trend.

The explanation of the variability of this parameter requires the analysis of the two important criteria for the biomass composition namely: the concentration of ash and moisture.

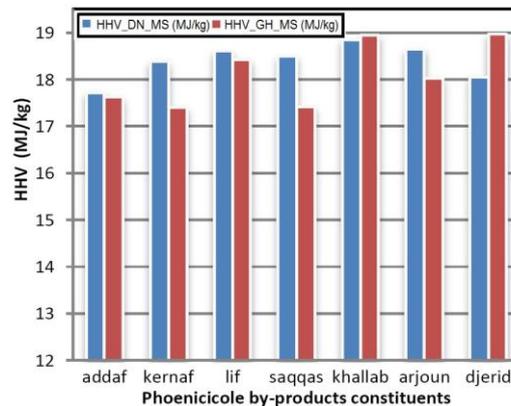


Fig. 4: Higher heating value HHV of cultivars GH and DN by-products in Guerrara oasis

Figures 5, 6, 7 show a comparison between these two parameters and the higher heating value HHV for each cultivar. An analysis of these figures shows an inverse correlation between the calorific value and moisture and ash concentrations especially for *khallab* case (DN and GH) and *kernaf* (GH). Equation 5, quoted by Navez (2002) [26] justifies the impact of mineral matter and moisture on the calorific value concentration:

$$\text{LHV} = 18400 \left( 1 - \frac{(\text{min})}{1 + (\text{H}_2\text{O})} \right) - 2500 \left( \frac{(\text{H}_2\text{O})}{1 + (\text{H}_2\text{O})} \right) \quad (1)$$

LHV, Low heating value (MJ/kg), (min), Mineral content (kg/kg DM); (H<sub>2</sub>O), Moisture (kg H<sub>2</sub>O/kg DM).

The effect of moisture is less important compared to the ash concentration on the calorific value. Cases of *djerid* (DN) and *saqqas* (GH) and the work of Navez *et al.*, (2002) [26] regarding the characterization of the biomass, Figure 7; confirms this conclusion.

This is explained by the fact that ashes have a significant impact on the pyrolysis combustion stage (key step in this process) because its products are the oxidation substrates (final stage of combustion).

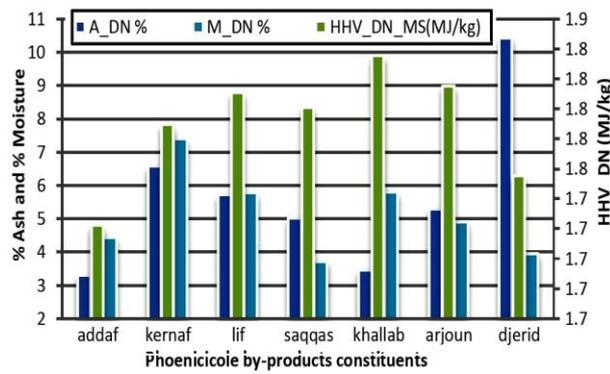


Fig. 5: Comparison between HHV , ash and the moisture of DN cultivar by-products

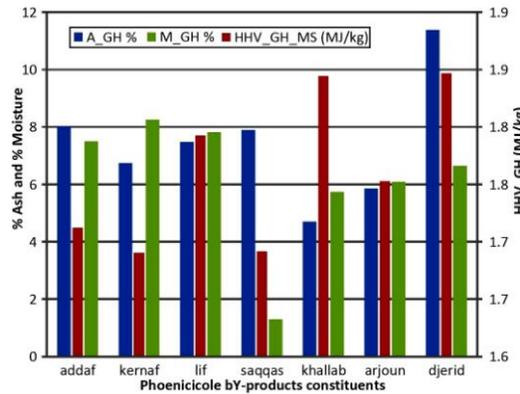


Fig. 6: Comparison between HHV , ash and the moisture of GH cultivar by-products

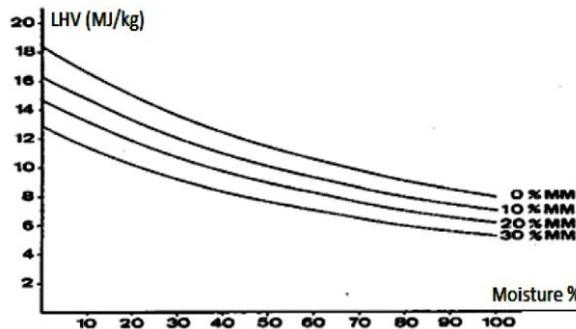


Fig. 7: Evolution of lignocellulosic materials low heating value LHV According to the moisture concentration and of minerals matter [26]

Exceptions may occur for the correlation between the by-products calorific value HHV and moisture and ash concentration. This is exactly the case of *djerid* (DN) where the ashes (clinker ashes) appear to have an inhibitory effect on the by-products calorific value HHV (Table 3), whereas for the case of *djerid* (GH), they have an opposite effect (catalytic) (Table 4).

Table 3: Correlation between the by-products calorific value HHV , ash and moisture for cultivar DN by-products

DN sub - products	HHV	Ash	Moisture
Djerid	↘	↗inhibiting	↘
Khallab	↗	↘	↘
Addaf	↘	↘	↘

↘: Low ↗: High ↘↘: Very low ↗↗: Very high

Table 4: Correlation between the by-products calorific value HHV , ash and moisture for cultivar GH by-products

GH sub - products	HHV	Ash	Moisture
Djerid	↗	↗catalytic	↘
Khallab	↗	↘	↘
Saqqas	↘	↗	↘
Kernaf	↘	↗	↗

↘: Low ↗: High ↘↘: Very low ↗↗: Very high

The average estimation of calorific value HHV (DM) of the entire biomass studied (~ 17.7 MJ/kg) is slightly lower than the calorific value of the biomass used as biofuels (**Table 5**) [16, 23]. This does not diminish the energy potential of the phoenicicole biomass studied which is interesting but must be combined with other criteria to determine the energetic behavior of this biomass.

**Table 5:** Higher heating value (MJ/kg) of various biomass [16, 23]

Leafytrees	PCS	Coniferous	PCS
Oak (duramen)	18,463	Pectinate fir tree	18,990
Oak (sapwood)	19,169	Spruce	19,195
Beech	18,802	Douglas (duramen)	19,165
Charm	18,735	Douglas (sapwood)	19,370
Ashtree	18,521	Maritime pine	19,165
Poplar	18,392	Woodland pine	20,946
Walnuttree	18,572	Larch	19,688
Acacia	19,015	Cedar (duramen)	20,984
Eucalyptus	17,773	Cedar (sapwood)	19,822
Phoenicicole syb-products	17,750	-	-

A calculation was conducted to determine the gross calorific value based on the immediate composition (volatile matter, ash and fixed carbon) of the considered biomass according to the equation [15]:

$$\text{HHV} = 0.3536 \times \text{FC} + 0.1559 \times \text{VM} + 0.0078 \times \text{A} \quad (2)$$

HHV, Higher heating value MJ/kg; FC, Fixed carbon %; VM, Volatile matter %; A: Ash %.

The approximation made in this formula appears interesting for palm tree wood's material. The calculation of the error by comparing the experimental determining method of the by-products calorific value PCS and the formula presented above is about 3% (**Table 6**). Thus, this formula could be retained for the determination of the gross calorific value of palm wood. This could be explained by the compatibility of the material used for the production of this formula with the considered by-products. Other approaches could be applied to this type of calculation (Dulong and Vandreak formula, {Eq. (8, 9)} [27]).

**Table 6:** Comparison between the calculated (HHV\_cal) and the experimental (HHV\_exp) by-products calorific value

HHV_cal_DN (MJ/kg)	HHV_exp_D N(MJ/kg)	Error %	PCS_cal_GH (MJ/kg)	HHV_exp_G H (MJ/kg)	Error %
17,2253	17,2219	0,02%	16,6778	17,1227	2,60%
18,3821	17,8924	2,74%	18,5381	16,9043	9,66%
17,8424	18,1053	1,45%	17,5455	17,9256	2,12%
18,0219	18,0065	0,09%	17,421	16,9168	2,98%
18,6865	18,3517	1,82%	18,6098	18,4432	0,90%
17,7704	18,1522	2,10%	18,2366	17,5267	4,05%
18,0656	17,5555	2,91%	16,8382	18,468	8,82%

### 3.4 Concentration of volatile matter and fixed carbon related to cultivars GH and DN by-products in Guerrara oasis

Figure 8 shows the concentration of volatile matter and fixed carbon in the various by-products (wastes) related to cultivars GH and DN in Guerrara oasis. The main findings include:

- The concentration of the fixed carbon for GH cultivar components ranges from 11.5% (*addaf*) to 19.9% (*kornaf*). It is estimated at an average of 16.2% (case of *lif*).
- Almost the same observations are made for DN variety with a variation of FC between 10.7% (in the case of *addaf*) and 20.3% (case of *djerid*). The average value for DN is estimated at 16.4%.
- For almost all the studied by-products, FC converges for both varieties with the exception of the cases of *arjoun* and *djerid* where a gap of more than 3% is found.
- The volatile matter concentration of cultivar DN by-products varies between 69.23% (case of *djerid*) and 85.95% (for *addaf*). The average value for DN is estimated at 77.87% (*khallab* case).
- In the case of GH cultivar, the volatile matter concentration of the by-products varies between 73.30% (*kernaf*) and 80.46% (*addaf*). The average value for GH is estimated at 76.34% (*khallab* case).
- The volatile matter of the majority of cultivar DN by-products are higher than GH cultivar's except DN's *djerid* with a value (69.23%) lower than GH's (73.30%).

It is worth reminding that the biomass fixed carbon is the carbon residue recovered after removal of volatile matter during pyrolysis step for about 10 min at 900 °C, as the following equation shows:

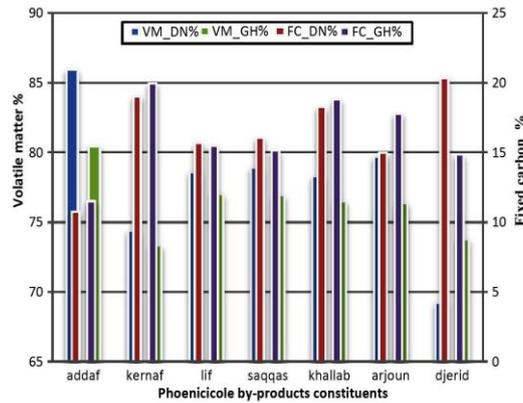


Fig. 8: Volatile matter and fixed carbon related to cultivars GH and DN by-products in Guerrara oasis

$$\text{Biomass} \rightarrow \text{Volatile matter} + \text{Fixed carbon} + \text{Ash} \quad (3)$$

Chemical energy is stored in our biomass in two forms: the volatile matter and fixed carbon. Figure 8 shows that despite some positive correlations between the fixed carbon concentration and the calorific value (case of *khallab* and *addaf* for DN and GH), this latter can only be interpreted as based on a combination of several factors essentially ash concentration. This interpretation is valid for volatile matter (Fig. 8).

A comparison between the concentration of volatile matter and the concentration of fixed carbon for different types of biomass with date palm by-products studied (Table 7) shows that they are closely similar to wood, straw and agricultural residues and therefore have the same assets in organic materials [16]. Nevertheless, treatments (carbonization and pyrolysis) are possible [28] to reach compatible proportions with coal's (fossil).

Table 7: Comparison from the CF and MV of various types of biomass [16] and the phoenicicole biomass

Various types of biomass	FC %			VM %		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Wood	18.5	12.3	26.3	78	69.5	86.3
Agricultural residues	19.1	12.4	37.9	75.2	59.3	85.5
Straw	17.1	13.6	19.5	74.3	64.3	80.5
All varieties of biomass	9.4	0.5	17.3	72.0	48.0	84.2
Animal biomass	13.6	/	/	55.5	/	/
Coal	46.3	20.0	71.8	32.8	12.4	51.8
Phoenicicole by-products	16.33	10.75	20.34	77.10	69.23	85.95

### 3.5 Elemental composition of different phoenicicole by-products from cultivars DN and GH

The elemental composition of the major phoenicicole by-products studied was calculated using the equations provided by Parikh *et al.*, (2004) [15],

$$\begin{aligned} C\% &= 0.637 \times FC + 0.455 \times VM \\ C\% &= 0.652 \times FC + 0.062 \times VM \\ O\% &= 0.304 \times FC + 0.476 \times VM \end{aligned} \quad (4)$$

C, Mass fraction of carbon %; H, Mass fraction of hydrogen %; O, Mass fraction of oxygen %; FC, Fixed carbon %; VM, Volatile matter %.

Figures 9 and 10 show the variation of three basic components (CHO %) compared with the calorific value PCS of the main by-products of cultivars DN and GH. The following observations:

- For the three basic components, we do not find a significant variation (standard deviation < 1 %).
- The percentage of the mass fraction of C related to the major GH cultivar's by-products varies between 43.02 % (*djerid* case) and 46.77 % (*khallab* case). The average value is estimated at 45.06 % (case of *lif*).
- The percentage of the mass fraction in O related to GH cultivar's main by-products varies between 39.62 % (*djerid* case) and 42.12 % (*khallab* case). The average value is estimated at 41.26 % (case *saqqas*).
- Finally, the percentage of the mass fraction in H of cultivar GH's main by-products varies between 5.34 % (*djerid* case) and 5.72 % (*khallab* case). The average value is estimated at 5.57 % (case of *lif*).
- The minimum values of the elemental composition are attributed to *djerid\_GH*'s by-products. While maximum values are attributed to *khallab\_GH* part.
- The percentage of the mass fraction of C major by-product DN cultivar varies between 44.45 % (*djerid* cases) and 47.24 % (case *khallab*). The average value is estimated at 45.89 % (case *addaf*).

- The percentage of the mass fraction in O of DN cultivar's main by-products varies between 42.06 % (case of *lif*) and 39.13 % (*djerid* case). The average value is estimated at 44.17 % (*addaf* case).
- Finally, the percentage of the mass fraction in H of cultivar DN's main by-products ranges from 5.35 % (case of *djerid*) and 5.88 % (*addaf* case). The average value is estimated at 5.68 % (in the case of *lif*).
- The minimum values of the elemental composition are attributed to *djerid*\_DN by-products. While maximum values are assigned to *addaf*\_DN part.
- Consistency (invariability) of the elemental constituents of phenolicole by-products of both cultivars can be explained by the combination of the biochemical composition of the biomass (cellulose content, hemicellulose and lignin) [29].

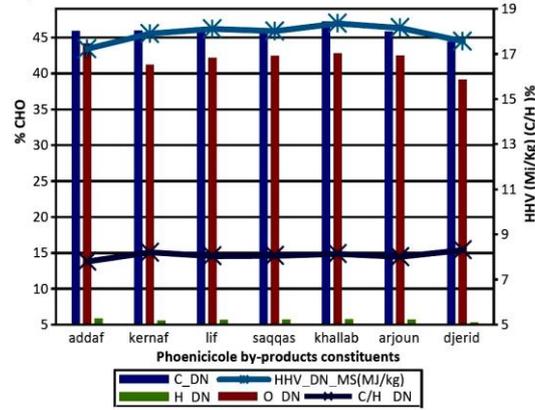


Fig. 9: Comparison between elemental composition and calorific value HHV of cultivar DN

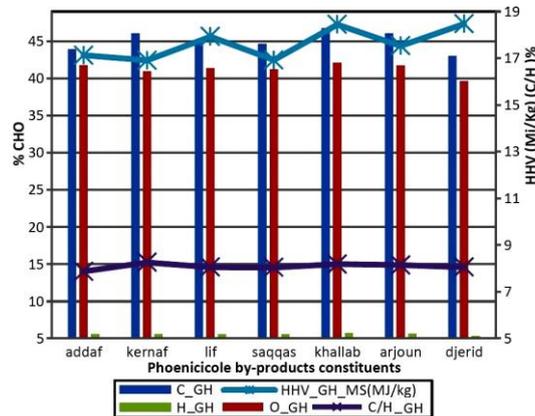


Fig. 10: Comparison between elemental composition and calorific value HHV of cultivar GH

The preceding figures show the positive correlation between the concentration of carbon and hydrogen and the quantity of energy that can be supplied by fuel (calorific value). Although the literature does not provide many models for calculating the calorific power in terms of the elemental composition, a literature review revealed three formulas confirming the correlations mentioned above. Considering some approximations:

- Using the rule of mixtures (heats of formation are insignificant compared to the heats of reaction).
- Assuming that all oxygen is already chemically combined, in fuel with hydrogen.
- The water concentration is only about the constituent water, i.e. water that is physically mixed with fuel

1) The gross calorific value can be calculated by the formula:

$$\text{HHV} = [\text{C}] \times \Delta h_{0\text{C}} + \{[\text{H}_2] - 1/8[\text{O}_2]\} \times \Delta h_{0\text{H}_2} + \Delta h_{0\text{S}} \times [\text{S}] - q_{\text{vap}} \times \{[\text{H}_2\text{O}] + 9/8[\text{O}_2]\} \quad (5)$$

In other words,

$$\text{HHH} = \text{enthalpie C} + \text{enthalpie H}_2 + \text{enthalpie S} - \text{water} \quad (6)$$

Either,

$$\text{HHV} = 32760 \times [\text{C}] + 120000 \times \{[\text{H}_2] - 1/8[\text{O}_2]\} + 9250 \times [\text{S}] - 2445 \times \{[\text{H}_2\text{O}] + 9/8[\text{O}_2]\} \quad (7)$$

2) Other calculation formulas, such as Dulong's and Vandralek's [27] which give respectively:

$$\text{HHV} = 4.18 \times (78.4 \times \text{C} + 241.3 \times (\text{H} - \text{O}/8) + 22.1 \times \text{S}) \quad (8)$$

$$\text{HHV} = 4.18 \times (85 \times \text{C} + 270 \times \text{H} + 26 \times (\text{S} - \text{O})) \quad (9)$$

Where: HHV, Higher heat value(kJ/kg);  $\Delta h$ , Enthalpy (kJ/kg); C: Mass percentage of carbon; H: Mass percentage of hydrogen; S: Mass percentage of sulphur; O: Mass percentage of oxygen.

A comparison of the elemental composition of biofuel with the main phoenicicole biomass (**Table 8**) shows a compatibility of this latter with agricultural residues overall [16].

**Table 8:** Comparison of the elementary composition of the various types of biomass [16]

Average composition (mass %)	C	H	O
Wood	52.1	6.2	41.2
Agricultural residues	49.9	6.2	42.6
Straw	48.	6	43.9
Ricestraw	48.2	6.5	45.1
Cotton stem	49.4	5.8	43.8
Thimbles of soya	45.4	6.7	46.9
Phoenicicole by-products	45.5	5.6	41.7

#### 4. GENERAL CONCLUSION

The Phoenicicole biomass is the backbone of the oasis ecosystem. The presentation of an overview of the chemical composition of phoenicicole biomass fuel in Guerrara oasis was the subject of this study, which leads us to the following conclusions:

- The biomass considered under this study has seven phoenicicole major by-products of palm date tree (*Phoenix dactylifera L.*): *djerid*, *addaf*, *kernaf*, *saqqas*, *arjoun*, *khallab* and *lif*. It is naturally dry through natural regeneration of the biomass on the tree, and contains very low moisture concentration (< 5 %). This criterion is very advantageous for storage and thermal conversion of biomass. The ash concentration of the considered phoenicicole by-products is relatively high (> 4.7 %) compared to conventional biofuels. It varies according to the part in question. This parameter has a significant effect especially on thermochemical processes. It has a significant effect on the biomass energetic capacity overall as it may catalyze or inhibit the reaction mechanisms of the thermochemical conversions. The gross calorific value (experimental) of the considered biomass in this study (~ 17 MJ / kg) is comparable to the known biofuels. This parameter varies according to the volatile matter, fixed carbon and the elemental composition. The latter is closer to the results reported in the literature, particularly those of agricultural waste and wood.
- The application of empirical model for the calculation of certain parameters (calorific value, mineral composition) may be interesting if they apply to materials whose composition is determined and compatible with the studied products. This is exactly the case of the calorific value for which, an error of about 3% was calculated (based on an empirical model).
- The conducting of immediate analyzes (moisture, volatile matter, fixed carbon, ash) and the determination of calorific value are a necessary first step for the study.

#### NOMENCLATURE

% , Percent	LHV , Lower heating
°C , Degree celcius	M , Moisture concentration
A , Ash concentration	Min , Mineral content, kg/kg
CF , Fixed carbon	MJ / kg , Mega joule per kilogram
DM , Dry matter	OPEC , Organisation of petroleum exporting Countries
DN , Deglet Nour cultivar	Qs , Quintaux
FAO , Food and Agriculture organization	TOE , Ton oil equivalent
GH , Ghars cultivar	URAER, Unité de Recherche Appliquée en En. Ren.
GGE , Greenhouse gas emission	VM , Volatile matter
HHV , Higher heating value	Xe , Carbon mass fraction %
kWh/kg , kilowatt hours per kg	XH Hydrogen mass fraction %
X <sub>0</sub> , Oxygen mass fraction	

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