AGRICULTURAL BY-PRODUCT RECYCLING IN THE PRODUCTION OF OILS AND BIODIESEL

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Four cultivars of Phoenix dactylifera L. from south-west of Algeria are exploited for the first time in the production of biodiesel. Physicochemical characteristics and fatty acid composition of these oils have been determined. The biodiesel is obtained by using acid transesterification of oils extracted from seeds of the fourth cultivars. Analysis by FT-IR spectroscopy confirmed the synthesis of biodiesels. GC-FID analysis has shown that the extracted oils can be classified as oleic-lauric oils, very rich in oleic acid C18:1 (44.74-47.99%) and lauric acid C12:0 (15.29-19.80%). In this study, we have valorized date seeds generally considered as waste. This valorization led to finished products: oil and biodiesel.

Keywords: Biodiesel, Oils, *Phoenix dactylifera* L., FT-IR, GC-FID

1. Introduction

Date palms allow a sustainable life in desert regions. Their fruits are excellent for health, and their marketing provides income for the owners [1,2]. Algeria has a favorable climate for development of date palms and fruits, particularly in the regions of Ouargla (Oued-Righ), Oued-Souf, Biskra (Zibans), Adrar (Touat, Gourara and Tidikelt) [2]. The propagation of date palm in Algeria, has marked an important progress in cultivars, which have reached 18 million palm trees, covering more than 350 000 ha, of which 11 million are productive [3,4]. Algeria is ranked 6th in the world, with an average annual production estimated at more than 492 000 tons of dates, which 70% consists of Deglet-Nour, Ghars, Degla-Beida and Mech-Degla varieties. It is ranked 5th for its exports and 1st for the quality of its exported Deglet-Nour fruit [5]. Adrar (South-west of Algeria) represented by three regions: Touat, Tidikelt and Gourara, is rich in 2.8

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million palm trees, which produce more than 91 360 tons of dates. Most of this production is exported to neighbor countries as barter; the rest is either consumed locally or used as livestock feed [4]. Contrary to palm groves of southeastern Algeria (Biskra, El-Oued and Ouargla), where there is a significant potential of very good quality cultivars (Deglet-Nour, Ghars, etc.). The phoenicultural patrimony of Adrar region is essentially made up of cultivars called "Khalts" (non-pure) strains such as H'mira, Tinaceur, Takerbouchet, Deglet-Talmine, etc. [6].

Cultivars are differentiated by the morphology of their main components: pericarps and seeds (stones). These represent 10-15% of date weight, depending on the variety and quality. According to FAO (2010), approximately 825 000 tons of date seeds are produced annually [7]. Hamada *et al*. 2002 have shown the composition of several date seeds as moisture, proteins, fats, acid detergent fibers, neutral detergent fibers and ash [8]. This composition opens up a spectrum of possibilities for the valorization of these seeds, including the extraction of oils and their transformation into biofuels [9]. Transesterification, which is a catalytic method, is the most suitable for converting oil into biodiesel. This product is a renewable biofuel that can be used in mixture with engine diesels [10]. According to the Organization for Economic Co-operation and Development (OECD) Food and Nations, the world production of biodiesel was about 36 billion liters in 2017. The European Union (EU) is still the largest producer with 13.5 billion liters, followed by the United States (6.9 billion liters) and Malaysia (490 million liters). The most widely used sources of production are palm, soybean and rapeseed oils [11]. The exploitation of date seeds will enable us to satisfy two objectives: one indirect of an environmental nature and the other direct, is about to obtain oils and biofuel. The environmental side will contribute to waste reduction. For this purpose, we report the exploitation of H'mira, Takerbouchet, Tegazza and Tinaceur as source of date seeds.

2. Materials and Methods

2.1. Chemicals

All the solvent were of reagent grade. n-hexane, Methanol, Potassium iodide, Potassium hydroxide and Sodium thiosulfate were purchased from BioChem. Starch, Sodium methanolate, Hydrochloric acid, Gallic acid and DPPH (2,2-Diphenyl-1-picrylhydrazyl) were obtained from Sigma Aldrich. Ethanol and Wijs reagent were purchased from Honewell and Fulka, respectively.

2.2. Sampling

Dates used in this work for the extraction of oil and biodiesel production were collected from the palm groves from: Zaouiet Kounta, 27°52’00”N,0°17’00”E (H’mira, (Hm)); Bouda, 28°00’51”N,0°30’09”E

(Takerbouchet, (Tk)) and from Reggane, 26°43’12”N,0°10’16”E (Tegazza, (Tg) and Tinaceur, (Tn)) (Fig. 1).

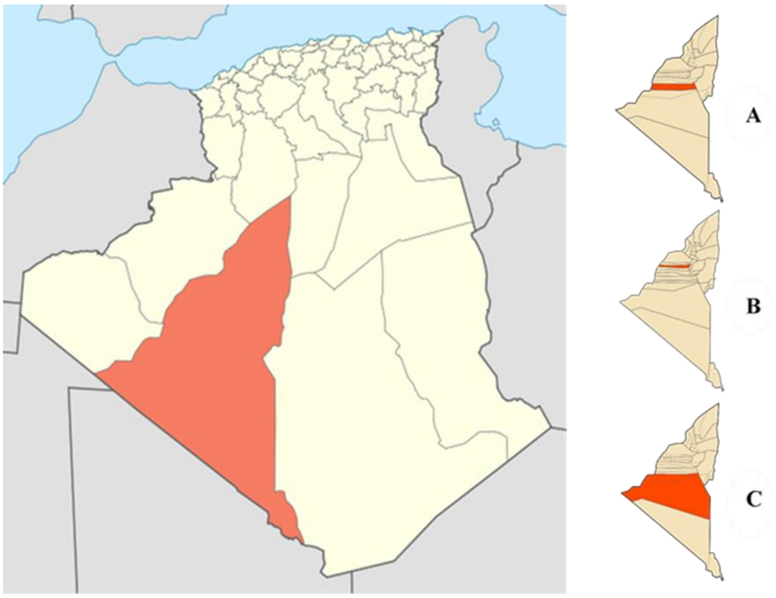

Fig. 1 Geographical location of Adrar region. Sampling regions: A) Zaouiet Kounta; B) Bouda; C) Reggane.

2.3. Date seeds preparation

Before using date seeds in the oil extraction process, they were left in boiling water with vigorous stirring for 3 hours to remove dust and residues. Subsequently, the separated seeds were washed several times with water, in order to remove stuck impurities, followed by drying at 105°C for 24 hours in an oven (Memmert type). The obtained seeds were crushed to 250 µm (Waring type).

2.4. Oil extraction

In a Soxhlet apparatus, 100 g of date seed powder from each cultivar are introduced and the extraction is carried out with 250 mL of n-Hexane for 4 hours. The extract is filtered to remove suspended particles. The bio-oil is then separated from the solvent by a rotary evaporator (Nahita type). The experiments were carried out in triplicate, and the oil content of each extraction was calculated as follows:

$$Oil\ content; \% = \frac{Oil\ mass\ obtained}{Mass\ of\ date\ seed} \times 100 \quad (1)$$

The obtained bio-oils were, labelled and stored in brown bottles at 4°C for further use.

2.5. Biodiesel production

A quantity of 20 g of the oil was heated in a round bottom tri-neck flask fitted with a reflux condenser and a thermometer. After 30 minutes of heating, an amount of 0.1 g of potassium hydroxide KOH (used as catalyst) dissolved in 60 g of methanol was added to the flask. The reaction took place for 90 minutes at the specified reaction temperature (55± 5°C) under reflux while the mixture was stirred simultaneously at 600 rpm. At the end of the reaction, Fatty Acids Methyl Esters (FAME) synthesized, were separated using a separating funnel. The methyl ester layer was freed of excess methanol by the rotary evaporator, followed by washing with lukewarm water (3×20 mL). The washed FAMEs are then dried by passage over sodium sulphate (Na_2SO_4), and biodiesel production yields were calculated as follows:

$$Yield;\% = \frac{Mass\ of\ produced\ biodiesel}{Mass\ of\ used\ oil} \times 100 \quad (2)$$

Biodiesels obtained were, labelled and stored in brown bottles at 4°C for analysis.

2.6. Physicochemical characterization

The key parameters to evaluate the properties and quality of oils or biodiesels are Saponification Value (SV), Acid Value (AV), Iodine Value (IV), Density (d), High Heating Value (HHV) and Cetane Index (CI). These parameters are widely used to determine purity (With SV), number of unsaturated compounds (With IV) and the content of Free Fatty Acids FFA (acidity%). Acid value (AV) indicates the corrosiveness of oil or biodiesel, while iodine value (IV) refers to the Degree of Unsaturation (DU). Similarly, gravity and specific density give the energy efficiency of a biofuel [12].

In this work, the density of the samples was measured at 20°C using a Pycnometer of 10 mL. The refractive index values were determined using a Refractometer (Abbe type). The chemical properties of our extracted oils and its biodiesels have been measured according to different official methods: Iodine value by the Wijs method (AOCS Tg-1a-64); Saponification value by (ASTM D5558-95), Acid value and free acidity (FFA %) by (ASTM D664-18e2).

Equation (3) described by Krisnangkura, 1986 [13], was used to calculate the cetane index (CI).

$$CI = 46.3 + 5458/(SV) - 0.225(IV) \quad (3)$$

HHV values were calculated using the empirical equation (4) suggested by Demirabs, 2008 [14].

$$HHV = 49.43 - [0.041(SV) + 0.015(IV)] \quad (4)$$

As previously mentioned, IV is the value that indicates the number of double bonds in oils. Therefore, it is also related to the Degree of Unsaturation DU of biodiesel [15].

$$DU = \sum [Monounsaturated\ FA + 2 \times (Polyunsaturated\ FA)] \quad (5)$$

According to Mofijur *et al*. 2017, when DU increases, IV also increases, indicating that the unsaturation in the sample will be higher. The equation (6) has been developed to predict the IV [15].

$$IV = (0.9076 \times DU) - 0.0527 \quad (6)$$

2.7. FT-IR Spectroscopic analysis

Analyses by FT-IR spectroscopy of extracted oils from seeds of Hm, Tk, Tg and Tn cultivars of Adrar region, and their biodiesels, were obtained using a Cary 660 FT-IR spectrometer (Agilent; USA) in the wave range of 4000-400 cm^{-1}, with a resolution of 4 cm^{-1}.

2.8. GC-FID analysis

Fatty acid composition of Hm, Tk, Tg and Tn seed oils was determined by gas chromatography (type GC TRACE 1300, Thermo Scientific, USA, equipped with a Flame Ionization Detector). One microliter of each biodiesel was injected with a split ratio of 1:18. Temperatures of Injector and Detector were 250 and 270°C respectively. Capillary column used is a Restek Rt-2560 type [length (100 m), film thickness (0.20 m), and internal diameter (0.25 mm)]. Hydrogen was used as carrier gas and was supplied at a rate of 1.5 mL/min. Oven temperature was 175°C for 5 min and then 2 °C/min at 185°C for 30 min. Analysis time was 40 min, and the chromatograms have been integrated in the range from C8:0 to C22:1 peaks. Fatty acid composition in any sample was considered as percentage area (%A) of peak.

3. Results and Discussion

3.1. Physicochemical properties of extracted oil

According to Table 1, the oil contents obtained (based on a dry weight), for all cultivars Hm, Tk, Tg and Tn are in 8-12% range. This is in agreement with values of extracted oils from other cultivars; such as Irakian *P. dactylifera* (5 and 13%) [16] and Saudi *P. Canariensis* (~10.36%) [17]. On the other hand, the majority of Saudi cultivars: Barhi, Khalas, Manifi, Ruzaiz, Sala and Soukari have oil contents lower than 8% [17,18]. Results given by Laghouiter *et al.* 2018, did not exceed 7% (max of 6.7% of Bint qbala cultivar in Laghouat region southeastern of Algeria) [19]. Specific density of the extracted oils in this study varies between 0.9117 and 0.9176 g/mL, which places them in same range of density values of vegetable oils, such as Sunflower (0.916 g/mL), Rapeseed (0.912 g/mL) and Soya (0.914 g/mL) [20]. The results related to the determination of IV showed values between 53.19 and 57.79 g I_2/100 g of oil. These values are much lower than those mentioned in other works such as Soya (134.9 g I_2/100g) [21], Moringa (79.23 g I_2/100g) [22] and Pumpkin seeds (113.2 g I_2/100g) [23]. This difference is an indicator of the texture of oils, which is similar to that of butter. Furthermore, and compared to the value cited by Fadhil *et al.* 2017 [16], which concerned the extraction of oil from seeds of Iraqi dates (IV= 47.66 g I_2/100g), the quality of oil from Algerian date seeds looks better. In addition, the results of SV indicate that the extracted oils are of acceptable quality.

Table 1

Physicochemical properties of extracted oil

Properties	Hm	Tk	Tg	Tn
Oil content (%)	8.41±0.25	11.25±2.39	9.49±0.89	7.97±1.09
Density at 20°C (g/mL)	0.9117±0.0032	0.9176±0.0012	0.9117±0.0105	0.9128±0.0002
Refractive index	1.4623±0.0005	1.4605±0.0003	1.4597±0.0051	1.4596±0.0003
Iodine value (gI_2/100 g)	53.19±1.32	57.79±2.85	55.73±2.38	56.28±2.11
Saponification value (mg KOH/g)	249.69±2.8	237.53±4.3	230.10±2.9	254.83±4.5
Acid value (mg KOH/g)	0.996±0.070	0.910±0.036	0.761±0.129	2.137±0.015
Free acidity, FFA%	0.507±0,035	0.458±0.018	0.383±0,065	1.076±0,007
Cetane index[a]	56.191	56.275	57.481	55.055
HHV[b] (MJ/kg)	38.395	38.824	39.160	38.138

[a] Cetane Index was calculated by a formula given by Krisnangkura, 1986 [13];
[b] Higher Heating Value was calculated by the formula given by Demirbas, 2008 [14];

Acidity values (AV) ranging from 0.761 to 2.137 mg KOH/g (Table 1), indicate that the triacylglycerol have not been hydrolysed. When the quality of the oil is taken into account, the quantity of FFA proves to be a good indicator. Indeed, oils, which have higher FFA contents, are of poor quality. FFA values, expressed as % of oleic acid, varied between 0.383 and 1.076%, which suggested a good quality of oils extracted from Hm, Tk and Tg cultivars, compared to oils obtained from Rapeseed (0.3-1.2%) [24], Olive (0.66-2.17%) [25] and sunflower oil (1.19-1.35%) [26], FFA value of oil suitable for edible purposes should not exceed 0.4% [27]. In fact, FFA values of Hm and Tn oils are outside of the nutritional limit (~0.4%).

3.2. Physicochemical properties of synthesized biodiesel

The production of FAME (biodiesel) from oils extracted from Hm, Tk, Tg and Tn seeds was achieved by methyl transesterification, using KOH as a catalyst. Table 2 gives us a general overview of different physicochemical properties of synthesized biodiesels. Yield conversions, of obtained biodiesels are not significantly different. It appears that biodiesel obtained from Tg oil has a high conversion (94.17%). In contrast, oil obtained from Tk variety gives 88% conversion. These results have been already reported in the literature (92.45%) [28].

The density allows us to situate the synthesized biodiesels within the required norms (NE 14214). In fact, the values of this parameter in our study vary between 0.87 and 0.89 g/mL, which is in accordance with the NE 14214 norm, which gives a limit value between 0.86 and 0.90 g/mL. Additionally, the density of petroleum diesel is about 0.85 g/mL, which is about 15 to 20% higher than the density of gasoline (0.70 to 0.75 g/mL). It is clear that the biodiesels synthesized in this study are more compliant, which justifies the good conversion of extracted oils, by removing the glycerol initially present. These results are confirmed by the lowering of the refractive index values (1.448-1.450), thus indicating the synthesis of biodiesels. Iodine Values (IV) and Acid Values (AV), according to Table 2, are in agreement with ASTM D6751 and EN 14214 norms, which leads to say that effectively the synthesized biodiesels are of acceptable quality. The maximal value of IV is 58.39 g I_2/100g (EN 14214; 120 g I_2/100g), and that of AV is 0.174 mg KOH/g (ASTM D6751 and EN 14214; 0.5 mg KOH/g).

Cetane index (CI) is one of the most important parameters to characterize a biodiesel. Indeed, a higher cetane number means that the fuel is more rapidly flammable [29]. We can see, from the results that the biodiesels resulting from the oils extracted are in accordance with international norms (ASTM D6751 and EN 14214).Values of CI are between 55 and 58, which confers them a very short ignition delay time. These same results were reported by İlkılıç *et al*. 2015 (*Pistacia Terebinthus*; CI= 55) [30] and Madiwale et Bhojwani, 2016 (Peanut; CI= 54) [31]. Finally, the calculated HHVs were within the international norms. The HHV calculated for biodiesel obtained from Tg cultivar is the highest (39,028 MJ/kg); which is in agreement with HHV reported in the work of Fadhile *et al*. 2017 (39.52 MJ/kg) [16] and Herch *et al*. 2014 (40.69 MJ/kg) [32]. The HHV (37.947-39.028 MJ/kg) obtained in this study are similar to biodiesels obtained from oil of Palm (37.20-39.91 MJ/kg), Soya (37.30-39.66 MJ/kg), Sunflower (37.50-39.95 MJ/kg) and Rapeseed (37.30-39.90 MJ/kg) [33].

Table 2

Physicochemical properties of synthetized biodiesels

Properties	Hm	Tk	Tg	Tn
Yield (%)	91.73±1.91	88.94±3.9	94.17±1.7	92.21±0.25
Density at 20°C (g/mL)	0.8785±0.0028	0.8865±0.0004	0.8781±0.0007	0.8725±0.0061
Refractive index	1.4488±0.0001	1.4500±0.0001	1.4468±0.0002	1.4479±0.0002
Iodine Value (gI_2/100 g)	53.54±1.85	58.39±1.69	54.27±1.07	55.48±1.21
Saponification Value (mg KOH/g)	252.33±1.5	239.52±2.1	233.85±1.8	259.77±3.2
Acid Value (mg KOH/g)	0.081±0.042	0.075±0.091	0.061±0.084	0.174±0.142
Free Acidity, FFA (%)	0.041±0.074	0.038±0.021	0.031±0.096	0.088±0.058
Cetane Index[a]	55.884	55.949	57.429	54.828
HHV[b] (MJ/kg)	38.281	38.734	39.028	37.947

[a] Cetane Index was calculated by a formula given by Krisnangkura, 1986 [13];
[b] Higher Heating Value was calculated by the formula given by Demirbas, 2008 [14];

3.3. FT-IR Spectra analysis

FT-IR spectra (Fig. 2) show a very intense band around 1745 and 1743 cm^{-1}. These bands correspond to the elongation vibrations of carbonyl groups; characteristic of extracted oils of Hm, Tk, Tg and Tn varieties. This same band is also visible in a spectrum corresponding to synthesized biodiesels, but this one is a characteristic of methyl esters. Bands situated around 1230-1234 cm^{-1} depending on the studied varieties, are due to the vibrations of asymmetrical elongation of C-O bonds of triacylglycerol in oils, the intensity of which is due to the presence of C=O groups. Moreover, the bands located at the same wavelengths in case of biodiesels are less intense, which allows us to say that the transesterification has been carried out successfully. The spectral analysis of oils extracted from Hm, Tk, Tg and Tn date seeds showed the existence of a band at 721-723 cm^{-1}, this band is resulting from the plane rotation of methylene groups for linear alkanes of four or more carbon atoms. This band is similar in the spectra of biodiesels, but of less intensity. Bands at ~3005 cm^{-1} and at 2922 /2852 cm^{-1} are assigned to the C_{sp^2}-H and C_{sp^3}-H vibrations (asymmetric and symmetric), respectively [34].

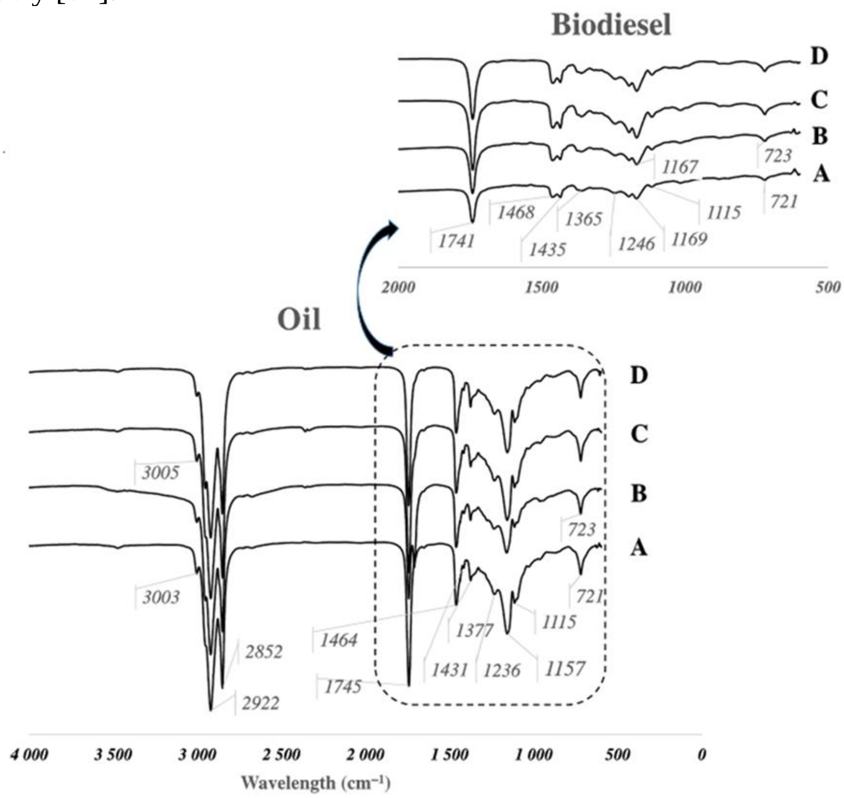

Fig. 2 FT-IR Spectrum, A: H'mira (Hm), B: Takerbouchet (Tk), C: Tegazza (Tg) and D: Tinaceur (Tn).

3.4. Fatty acids composition

Table 3 shows the fatty acid composition of the four cultivars Hm, Tk, Tg and Tn, where 10 fatty acids have been identified, representing 71.43% of the total fatty acids identified in the date seeds of cultivars cited in literature (as a number of 14) [35]. The major fatty acids in the seeds of Hm, Tk, Tg and Tn cultivars are Lauric acid C12:0 (15.2-19.8%), Myristic acid C14:0 (10.6-11.5%), and Palmitic acid C16:0 (11.2-13.2%). These Saturated Fatty Acids (SFA) have several health effects according to various medical studies [12]. Oleic acid C18:1 (44.7-47.99%), which is an Omega 9 FA, has apparent beneficial effects on cardiovascular risks by decreasing the rate of LDL lipoproteins (bad cholesterol), and increasing the rate of HDL (good cholesterol) [36]. This acid is otherwise, considered as an important source to replace animal fats, which are rich in SFA [37]. Other acids have been identified with rates varying between 7.5 and 8.9% attributed to the presence of Z, Z-Octadeca-9,12-dienoic (Omega 6 FA). The presence of these acids shows the nutritional interest of oils extracted from date seeds, which are considered as a non-recoverable waste.

In general, and in this work, it is shown that the rates of saturated fatty acids (43.09 and 46.21%) are lower than the rates of unsaturated fatty acids (52.41-55.58%), which gives added value to these oils extracted from H'mira, Takerbouchet, Tegazza and Tinaceur cultivars. These results are in agreement with DU values (60.08-67.06), as well as calculated (54.47-60.81 g I_2/100g) and measured (53.54-58.39 g I_2/100g) of iodine values. The rates of unsaturated fatty acids are similar to those of oils extracted from Deglet-nour, Allig and Bellah cultivars, cited by Ben-youcef *et al*. 2017 [35]

Table 3

Fatty Acids Composition

Fatty Acid	Notation	Hm	Tk	Tg	Tn	PO[a]
Caprylic	C8 :0	0.287	0.136	0.212	0.230	–
Capric	C10 :0	0.405	0.251	0.347	0.320	0.35
Lauric	C12 :0	19.803	15.297	17.959	17.197	0.12
Myristic	C14 :0	11.393	11.512	11.221	10.663	1.36
Palmitic	C16 :0	11.285	13.251	11.590	11.399	42.75
Palmitoleic	C16 :1	0.0	0.181	0.033	0.0	0.0
Stearic	C18 :0	3.041	3.152	3.509	3.282	4.64
Oleic	C18 :1	44.736	45.975	45.579	47.994	39.33
Linoleic	C18 :2	7.676	8.955	7.881	7.585	10.37
α–Linolenic	C18 :3	0.0	0.0	0.0	0.0	0.41
Saturated FA		46.215	43.599	44.838	43.090	49.22
Monounsaturated FA		44.736	46.155	45.612	47.994	39.22
Polyunsaturated FA		7.674	8.955	7.881	7.585	10.78
Others		1.375	1.291	1.670	1.330	0.78
Total		100.0	100.0	100.0	100.0	100.0
DU		60.084	67.065	61.374	63.164	60.78
IV Calculated		54.473	60.815	55.650	57.275	55.11
IV Measured		53.54	58.39	54.27	55.48	-

Hm : H'mia ; Tk : Takerbouchet, Tg : Tegazza, Tn : Tinaceur, DU : Degree of Unsaturation, IV : Iodine Value.

[a] Palm Oil [37].

4. Conclusions

Oils were extracted from seeds of four cultivars of the date palm *P. dactylifera* L., provided from Adrar region, and a biodiesel was synthesized from each oil. The composition of the oils revealed the presence of unsaturated fatty acids giving an important nutritional value, and the possibility of their valuation as biodiesel by the transesterification process. The quality of the biodiesels obtained, rivals the biodiesels produced by common oils (palm, soybeans, etc.), taking into account their physicochemical properties. Finally, we can conclude that from an environmental strategy point of view, this study is very interesting because of the reduction in waste from date palms, which are valued as cheap energy sources and more respectful of the environment.

R E F E R E N C E S

[1]. *A.A. Mariod, M.E.S. Mirghani and I. Hussein*, "*Phoenix dactylifera* date palm kernel oil", In: A.A. Mariod, M.E.S. Mirghani and I. Hussein. (eds) Unconventional oilseeds and oil sources. Academic Press, USA, 2017, pp. 181–185.

[2]. *Allam Abdelkader*. Etude de l'évolution des infestations de palmier dattier (*Phoenix dactylifera* Linné, 1973) par *Parlatoria blanchardi* Targ. (*Homoptera diaspididae* Targ. 1892) dans quelques biotopes de la région de Touggourt, PhD Thesis, National Agronomic Institute, El-Harrach Algiers, 2008.

[3]. *A. Habchi, S. Kalloum and L. Baradai*, "Follow the degradation of organic matter during composting of date palm (*phoenix dactylifera* L) waste by physicochemical properties, UV-visible and FT-IR analysis", in J. Envir. Anal. Chem., 2020. Doi: 10.1080/03067319.2020.1761347.

[4]. *A. Boulal, A.E. Atabani, M.N. Mohammed, M. Khelafi, G. Uguz, S. Shobana and G. Kumar*, "Integrated valorization of Moringa oleifera and waste *Phoenix dactylifera* L. dates as potential feedstocks for biofuels production from Algerian Sahara: An experimental perspective", in Biocata. Agri. Biotech., 2019, pp.101234.

[5]. *A. Chehma and H.F. Longo*, "Valorization of date palm by-products for use in livestock feed", in Rev. Energ. Ren. : Produc. Valori. – Bioma., 2001, pp. 59–64.

[6]. *A. Zaki, A. Tirichine, A. Laaboudi, B. Moussaoui and M. Khersi*, "Knowledge of genetic resources of date palm in the region of Adrar (Touat, Gourara and Tidikelt)", in Acta Horticulturae, **vol. 994**, 2013, pp.125–131.

[7]. *M. Al-Farsi, C. Alasalvar, A. Morris, M. Baron and F. Shahidi*, "Comparison of antioxidant activity, anthocyanins, carotenoids, and phenolics of three native fresh and sun-dried date (*Phoenix dactylifera* L.) varieties grown in oman", in J. Agri. Food Chem., **vol. 53**, 2005, pp. 7592–7599.

[8]. *J. Hamada, I. Hashim and F. Sharif*, "Preliminary analysis and potential uses of date pits in foods", in Food Chemistry, **vol. 76**, no. 2, 2002, pp. 135–137.

[9]. *M. Karvonen and K. Klemola*, "Identifying bioethanol technology generations from the patent data", in World Pat. Inf., **vol. 57**, 2019, pp. 25–34.

[10]. *M.W. Mumtaz, A. Adnan, H. Mukhtar, U. Rashid and M. Danish*, "Biodiesel production through chemical and biochemical transesterification", In: M.G. Rasul, A.K. Azad and S.C. Sharma. (eds) Clean energy for sustainable development. Academic Press, USA, 2017, pp. 465–485.

[11]. *R.V. Quah, Y.H. Tan, N.M. Mubarak, M. Khalid, E.C. Abdullah and C. Nolasco-Hipolito*, "An overview of biodiesel production using recyclable biomass and non-biomass derived magnetic catalysts", in J. Envir. Chem. Engi., 2019. DOI:10.1016/j.jece.2019.103219.

[12]. *A. Astrup, F. Magkos, D.M. Bier, J.T. Brenna, M.C. de Oliveira Otto, J.O. Hill, J.C. King, A. Mente, J.M. Ordovas, J.S. Volek, S. Yusuf and R.M. Krauss*, "Saturated fats and health: a reassessment and proposal for food-based recommendations: JACC State-of-the-Art review", in J. Am. Coll. Cardiol., 2020. DOI:10.1016/j.jacc.2020.05.077

[13]. *K. Krisnangkura*, "A simple method for estimation of cetane index of vegetable oil methyl esters", in J. Am. oil Chem. Soc., **vol. 63**, 1986, pp. 552–553.

[14]. *A. Demirbas*, "Relationships derived from physical properties of vegetable oil and biodiesel fuels" in Fuel, **vol. 87**, no. 8-9, 2008, pp. 1743–1748.

[15]. *M. Mofijur, M.G. Rasul, N.M.S. Hassan, H.H. Masjuki, M.A. Kalam and H.M. Mahmudul*, "Assessment of physical, chemical, and tribological properties of different biodiesel fuels. clean energy for sustainable development", In: M.G. Rasul, A.K. Azad and S.C. Sharma. (eds) Clean energy for sustainable development: comparisons and contrasts of new approaches. Academic Press, USA, 2017, pp. 441–463.

[16]. *A.B. Fadhil, M.A. Alhayali, L.I. Saeed*, "Date (*Phoenix dactylifera* L.) palm stones as a potential new feedstock for liquid bio-fuels production", in Fuel, **vol.** 210, 2017, pp. 165–176.

[17]. *I. Nehdi, S. Omri, M.I. Khalil and S.I. Al-Resayes*, "Characteristics and chemical composition of date palm (Phoenix canariensis) seeds and seed oil", in Ind. Crop. Prod., **vol. 32**, no. 3, 2010, pp. 360–365.

[18]. *I.A. Nehdi, H.M. Sbihi, C.P. Tan, U. Rashid and S.I. Al-Resayes*, "Chemical composition of date palm (*Phoenix dactylifera* L.) seed oil from six saudi arabian cultivars" in J. Food Sci., **vol. 83**, no. 3, 2018, pp. 624–630.

[19]. *O.K. Laghouiter, M. Benalia, N. Gourine, A. Djeridane, I. Bombarda and M. Yousfi*, "Chemical characterization and in vitro antioxidant capacity of nine Algerian date palm cultivars (*Phoenix dactylifera* L.) seed oil", in Mediterranean J. Nutri. Metab., **vol. 11**, no. 2, 2018, pp.103–117.

[20]. *M. Mancini, M. Lanza-Volpe, B. Gatti, Y. Malik, A.C. Moreno, D. Leskovar and V. Cravero*, "Characterization of cardoon accessions as feedstock for biodiesel production", in Fuel, **vol. 235**, 2019, pp. 1287–1293.

[21]. *Z. Zhang, Q. Xie and L. Che*, "Effects of gamma irradiation on aflatoxin B 1 levels in soybean and on the properties of soybean and soybean oil" in Appl. Radiat. Isot., **vol. 139**, 2018, pp. 224–230.

[22]. *B. Oladipo and E. Betiku*, "Process optimization of solvent extraction of seed oil from *Moringa oleifera*: An appraisal of quantitative and qualitative process variables on oil quality using D-optimal design" in Biocatal. Agric. Biotechnol., **vol. 20**, 2019, pp. 101187.

[23]. *M.Z. Amin, T. Islam, F. Mostofa, M.J. Uddin, M.M. Rahman and M.A. Satter*, "Comparative assessment of the physicochemical and biochemical properties of native and hybrid varieties of pumpkin seed and seed oil (*Cucurbita maxima* Linn.)", in Heliyon, **vol. 5**, no. 12, 2019, e02994.

[24]. *S.M. Ghazani and A.G. Marangoni*, "Minor components in canola oil and effects of refining on these constituents: A review", in J. Am. Oil Chem. Soc., **vol. 90**, no. 7, 2013, pp. 923–932.

[25]. *C.C. Osawa, L.A.G. Gonçalves and S. Ragazzi*, "Correlation between free fatty acids of vegetable oils evaluated by rapid tests and by the official method", in J. Food Compos. Anal., **vol. 20**, no. 6, 2007, pp. 523–528.

[26]. *A.A. Gotor and L. Rhazi*, "Effects of refining process on sunflower oil minor components: a review", in OCL, **vol. 23**, no. 2, 2016, D207.

[27]. *I.A. Amoo*, “Effect of roasting on the chemical composition of coconut (*Cocos nucifera*) seed flour and oil”, in J. Food Agri. Environ., **vol. 2**, no. 3-4, 2004, pp. 18–20.
[28]. *Z.I. Jibril, A. Ramli, K. Jumbri and N. Mohamad Yunus*, “*Phoenix dactylifera* L. seed pretreatment for oil extraction and optimization studies for biodiesel production using Ce-Zr/Al-MCM-41 catalyst”, in Catalysts, **vol. 10**, no. 7, 2020, pp. 764.
[29]. *S. Geacai, I. Nita, O. Iulian and E. Geacai*, “Refractive indices for biodiesel mixtures”, in U.P.B. Sci. Bull., Series B, **vol. 74**, no. 4, 2012, pp. 149–160.
[30]. *C. İlkılıç, E. Çılğın and H. Aydın*, “Terebinth oil for biodiesel production and its diesel engine application”, in J. Energy Inst., **vol. 88**, no. 3, 2015, pp. 292–303.
[31]. *S. Madiwale and V. Bhojwani*, “An overview on production, properties, performance and emission analysis of blends of biodiesel”, in Procedia Technol., **vol. 25**, 2016, pp. 963–973.
[32]. *W. Herch, H. Kallel and S. Boukhchina*, “Physicochemical properties and antioxidant activity of tunisian date palm (*Phoenix dactylifera* L.) Oil as affected by different extraction methods”, in Food Sci. Technol., **vol. 34**, no. 3, 2014, pp. 464–470.
[33]. *K. Zahan and M. Kano*, “Biodiesel production from palm oil, its by-products, and mill effluent: A review”, in Energies, **vol.** 11, no. 8, 2018, pp. 2132.
[34]. *D. Gingasu, I. Mindru, O.C. Mocioiu, S. Preda, N. Stanica, L. Patron, A. Ianculescu, O. Oprea, S. Nita, I. Paraschiv, M. Popa, C. Saviuc, C. Bleotu and M.C. Chifriuc*, “Synthesis of nanocrystalline cobalt ferrite through soft chemistry methods: A green chemistry approach sesame seed extract”, in Mater. Chem. Phys., **vol. 182**, 2016, pp. 219–230.
[35]. *S. Ben-Youssef, J. Fakhfakh, C. Breil, M. Abert-Vian, F. Chemat and N. Allouche*, “Green extraction procedures of lipids from tunisian date palm seeds”, in Ind. Crop Prod., **vol. 108**, 2017, pp. 520–525.
[36]. *X. Bi, P.C. Siow, S.W. Lim and C.J. Henry*, “Dietary fatty acids analysis and its relevance to human health”, in SM J. Nutr. Metab., **vol.** 1, no. 1, 2015, pp. 1005.
[37]. *A. Rohman and Y.B.C. Man*, “Fourier transformed infrared (FTIR) spectroscopy for analysis of extra virgin olive oil adulterated with palm oil”, in Food Res. Int., **vol. 43**, no. 3, 2010, pp. 886–892.