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Conference paper

Valorisation of Algerian agro-wastes as renewable biofuels: Impact of using microwave-assisted method on lipid extraction

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ABSTRACT

Fossil fuels are the largest contributor to climate change, representing about 90% of carbon dioxide emissions. Given the environmental impact and the high prices around the world, finding an alternative solution has become necessary at the present time. Biodiesel, as a renewable energy, is considered one of the possible solutions to reduce these emissions since the CO2 emitted during combustion will be recycled again by nature for feedstock production. This process is known as a closed carbon cycle. The cost of producing biodiesel depends on the nature of the raw material and the production method which involves both oil extraction and its transformation to biodiesel. Our contribution lies in feedstocks choice and extraction method, namely, we provide a comparison between conventional extraction methods including maceration, Soxhlet and microwave-assisted extraction as an innovative method. The latter technique has been developed for the extraction of lipids from different agro-wastes available in Algeria. Our results show that MAE of lipid has proven its effectiveness in terms of rapid and powerful heating, particularly regarding extraction time, which was 1/6 and 2/3 of SE and ME extraction time respectively. The use of different extraction method has no obvious impact on the presence of functional groups, between dates' palm seeds and olive pomace lipids. However, it can be more significant when using ME.

1. INTRODUCTION

Earth's temperature has increased by around 1.1°C during the past ten years *(Lenssen et al. 2019; GISTEMP)*, making it the warmest decade overall. With a production reaching 1.015 million barrels per day in 2022 *(World Meteorological Organization)*, Algeria is listed among the nations whose economies are heavily dependent on petroleum energy. This places it among the top twenty oil-producing countries

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in the world *(International Energy Agency)*. Researchers have recently focused their attention on renewable energies as an alternative of achieving sustainability with less environmental inconvenience. E.g. biodiesel, a monoalkyl ester consisting of long-chain fatty acids sourced from both edible and non-edible vegetable oils or animal fats *(Knothe, 2006; Nakpong & Wootthikanokkaahan, 2010; Boulal et al. 2022a; Hidouri & Mouftahi, 2022; Bessah et al. 2023)*.

In order to improve the competitiveness of biodiesel against conventional diesel, it is therefore imperative to explore cheaper non-edible raw materials. Our attempt is to use two types of agro-wastes found in Algeria, and to investigate the possibility of valorising them to produce alternative fuel energy. The raw material type was chosen on the basis of its availability in Algeria and its ability for recycling and utilisation in biodiesel production. In our study we proposed using olive pomace (OP) and date palm seeds (DPS) as candidate agro-wastes.

Pomace is a solid by-product resulting from olive oil extraction. It is estimated that the annual amount of pomace generated in Algeria is 162000 t. Our estimation is based on the available data provided by the International Olive Council (IOC) reports 2022-2023 regarding the total olive oil production, and on the assumption that, using the press method, each 1 t of olive-oil produced, results in 2 t of by-products pomace *(Bakhouche et al. 2023)*.

The other agro-waste we are proposing is DPS. The Maghreb subregion accounts for 18.8% of world's total production of dates *(Food and Agriculture Organization)*. Algeria contributed with 1029596 Mt of production in the year 2016 alone *(Akbi et al. 2017)*, i.e. large amounts of date waste is available, and consequently good opportunities for valorisation are present.

Additionally, the choice of oil extraction method can also help to make the prices of these vegetable oils more competitive. Even though the most common traditional extraction methods used toxic solvent in large quantities, not to mention the extended extraction duration. These traditional methods are less effective compared to microwave-assisted extraction (MAE) due to the rapid and uniform heating added to cellular structure destruction in plant tissues provided by microwave irradiation *(Ferrera et al. 2023; Regier, 2014; Leone et al. 2014; Azadmard-Damirchi et al. 2010; Chenmat et al. 2005)*.

The purpose of this study is to assess the usefulness of MAE as a more cost-effective lipid extraction for two potential feedstocks. As a standard approach, oils are also extracted using conventional extraction including Soxhlet (SE) and maceration (ME). It is worth to mention that in our MAE experiments, we used microwave radiation to only heat the solvent, while keeping the sample outside the microwave cavity, as will be explained in more details in Section. 2.

2. MATERIALS AND METHODS

2.1 Sample preparation

Olive pomace: olive pomace was obtained from traditional olive mill located in Tizi Ouzou (Algeria). The olive cake material, freshly collected during the olive harvest season (November to December 2023), was subjected to the following pre-treatment steps:

- Drying in an oven for 1 h at a temperature of 105°C.
- Grinding using Herb and spice grinder (200 G-HR 200).
- Sieving of the ground powder using an electric sieve shaker, in order to select the particle size of 0.5−1 mm.

Dates seeds: the dates' stones were separated by hand from the fruits of the variety Moukentichi, collected from farmlands in Biskra, Algeria in 2023. The date kernels underwent some pretreatments as follows:

– cleaning under the water in order to remove the peels.
– Air-drying for 45 days in shadow.
– Grinding using the same grinder mentioned above used for olive pomace.
– Separating the particle size in the range of 0.5−1 mm by sieving the ground dates kernels using an electric sieve shaker.

Both samples (olive pomace and dates kernels, see Fig. 1) were kept in freezer until use.

Fig 1. Olive pomace and dates kernels used in this study.

2.2 Determination of moisture content

The two samples had been subjected to drying for 24 h in a vacuum oven at 100°C until a constant weight was achieved for the two samples. The moisture content was calculated according to the formula $MC_{\text{wet basis}}=(m_w\text{-}m_d)/m_w$, where $MC_{\text{wet basis}}$ is the moisture content on a wet basis (g/g), and m_w and m_d are respectively the wet and dried weights of the sample (expressed in units of g).

2.3 Lipid extraction process

Lipid extraction with Soxhlet (SE), maceration (ME), and MAE were carried out using a mixture of polar and non-polar organic solvents (ethanol and hexane). All extraction experiments were performed in triplicate, except the extraction of olive pomace in SE and MAE where duplicate experiments were considered. Table 1 gives the conditions for the performed experiments in our study for each of the extraction methods used.

Soxhlet extraction: 50 g of each powder of date seeds palm and olive pomace were weighed and transferred to a cellulose thimble. This latter is placed in the extraction chamber of a 300 mL Soxhlet apparatus fitted at the top with a condenser and at the bottom with a 500 mL distillation flask containing 250 mL of solvents mixture (hexane/ethanol).

Maceration: In extraction beaker, 20 g of the dried ground samples were placed in contact for 1 h under agitation using a magnetic stirrer at 35°C with 100 mL of solvents mixture (hexane/ethanol).

Microwave-assisted extraction: A household microwave oven (Boommax) was modified in our laboratory by placing the distillation flask from the Soxhlet apparatus inside the microwave oven while the remaining parts of the apparatus on the top (see Fig. 2). Moreover, controlling switching the microwave oven on and off is done with the help of an Arduino board (Arduino Uno board). The oven produces microwaves with power of 700 W, which was irradiating the suspension (solvents). The Arduino is programmed to turn the microwave oven on for a duration of 5 s, then turn it off for 10 s. The total duration of the experiment was set to 2 h.

Table 1. Experimental conditions and lipids yield for different extraction method.

	MAE	**SE**	**ME**
Solvent type (1:1)	hexane/ethanol	hexane/ethanol	hexane/ethanol
Time (min)	40	240	60
Solvent to weigh ratio (g/mL)	1:5	1:5	1:5
Temperature (°C)	Mixture boiling point	Mixture boiling point	35
Power (W)	700	/	/
Lipid yields (DPS)	6.580 ± 0.004	9.200 ± 0.002	11.06 ± 0.01
Lipid yields (OP)	5.000 ± 0.004	13.070 ± 0.002	6.71 ± 0.01

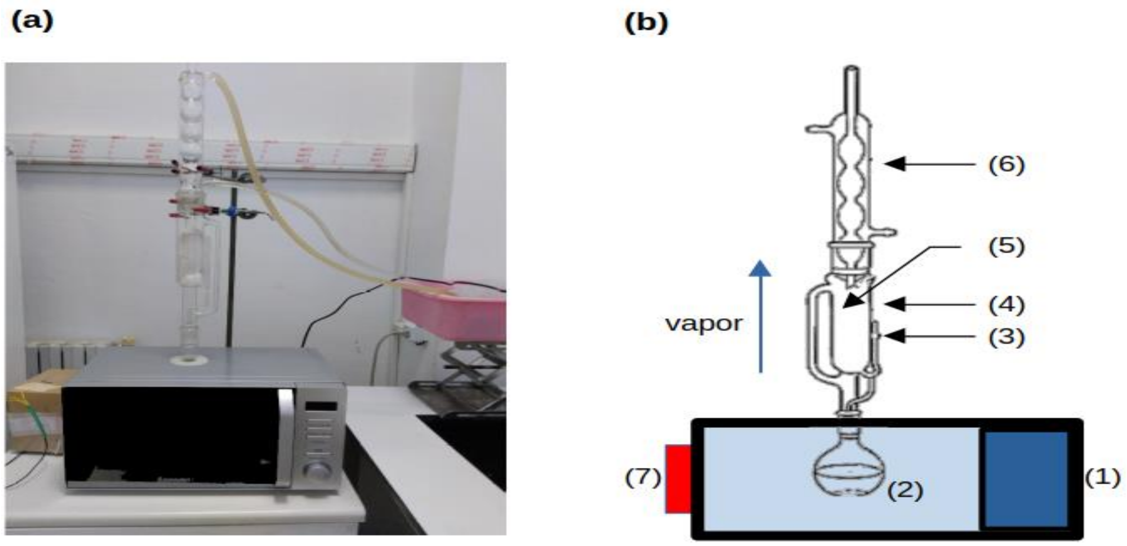

Fig 2. Microwave-assisted extraction system. (a) actual setup, (b) schematics: (1) microwave oven, (2) solvent, (3) siphon arm, (4) thimble, (5) extraction chambre, (6) condenser, (7) Arduino board.

At the end of the operation, the solvents were evaporated using rotary evaporator in such a way as to separate lipids from the obtained extract (lipid + solvents residue) in the distillation flask. Finally, the obtained oil was weighted and stored in deep freezer at −4°C.

The yield of the obtained lipids for each extraction was calculated using the equation Yield (%) = W_{lipid}/W_{DM}, where W_{lipid} and W_{DM} are the weight of the extracted lipids and the weight of the dry raw matter sample respectively.

3. RESULTS AND DISCUSSION

3.1 Moisture content

The moisture content with other volatiles in DPS was found equal to 2% which is close to that found for Iranian DPS *(Dehdivan & Panahi, 2017)*. The olive pomace showed 6% of moisture and volatiles. These low contents of moisture can be due to the fact that the used seeds were well dried.

3.2 Lipid yield

Table 1 depicts the extracted lipids from both of feedstock (OP and DPS) using various methods (MAE, SE and ME), in order to study the effectiveness of innovative methods on the quantity and quality of extracted oils. For OP, extraction by the Soxhlet method gives a yield of 13.07%. Previous works *(Koubaa et al. 2017; Ferarsa & Moulai-Mostefa, 2019)* confirm this result, where it was found the value of 12.0 ± 0.2 % and 15.19 ± 0.23 % from Algerian olive pomace within 6 h. As for DPS a lipid yield of 9.2% is found, which is close to the results of *(Ali et al. 2015)*, with a record of 8.5 % using 0.425 mm of particle size within 2 h of extraction. On the other hand, using the maceration technique appears more effective for DPS, unlike OP giving 11.06% and 6.71% respectively.

According to our results, for DPS and OP respectively the yield can easily reach two thirds and a quarter of the SE lipid yield with a MAE extraction that takes less than 1/6 of the SE extraction time. This was confirmed in a study *(Yanik,2017)* where the OP oil was extracted using MAE in shorter time (16 min) with higher yield compared to conventional extraction technique (120−180 min). In another research *(Ben-Youssef et al.2017)*, several types of dates palm seeds (Deglet Nour, Allig, and Belah) were used, where the extraction time was 30 min using ultrasound and microwaves compared to Soxhlet method (8h).

While the DPS and OP derived lipids produced through the use of microwaves in 40 min represent respectively 60% and 74% of those extracted by ME after 60 min, even if the yield recorded by ME is importantly increased by the presence of alcohols or phenols especially in the case of DPS lipids. This presence was detected by the peak of 3399 cm−1 in the FTIR ME spectra for the two raw materials (see Fig. 3). Therefore, compared to ME and SE, the efficiency of using microwaves lies mainly in the reduction of extraction time.

Several researches also showed that the OP and DPS are good candidates for the biodiesel manufacturing *(Boulal et al. 2022a; Ferarsa & Moulai-Mostefa, 2019; Touati, 2013; Ozçelik et al. 2020; Ayas et al. 2019; Rajaeifar et al. 2016; Lama-Munoz et al. 2014; Boulal et al. 2022b; Mekonnen & Sendekie, 2021; Al-Mardeai et al. 2023; Giwa et al. 2021; Allami et al. 2023)*. There are certain indicators within the biodiesel giving its quality. Obviously, these indices depend on the characteristics of the source oil used to produce it. One indicator is the acid index which indicates the oil content originating from free fatty acids. It had been found in *(Ferarsa & Moulai-Mostefa, 2019)* that OP oil has acid index of 41.73 mg/g of KOH. Another study *(Touati, 2013)* found the value 52 mg/g of KOH for OP, which is richer in FFA than DPS oil of Deglet-Nour, Ghars, and Tamdjouhert obtained from Ouargla region in Algeria (1.35, 1.36, 1.38 mg/g of KOH for DPS respectively *(Boulouada, 2009)*).

Another indicator for diesel quality is the density of the source oil. It was found in *Abollé et al. 2009)* that the high density of oil effect on diesel engines where vegetable oils exhibit greater inertia compared to gas oil at equivalent injection pressures. The density found in *(Ferarsa & Moulai-Mostefa, 2019)* and *(Touati, 2013)* (0.91 g cm^{-3}) is comparable to the density of Jatropha oil (0.867 g cm^{-3}) *(Aigba, 2021)*.

The oil's viscosity significantly rises with the presence of free fatty acids. The viscosity of OP oil found in *(Ferarsa &Moulai-Mostefa, 2019)* (34.758 mm^2 s^{-1}) is less than the one found in *Touati, 2013)* (63.05

mm^2 s^{-1}). These values are higher than the viscosity of Jatropha oil *(Aigba et al. 2021)* (28.43 mm^2 s^{-1}). The OP value could be reduced by the saponification of oil prior to transformation to biodiesel *(Mehdaoui et al. 2023)*. The physical and chemical properties of the methyl ester produced from DPS *(Azeem et al. 2016)* and OP *(Ferarsa &Moulai-Mostefa, 2019; Touati, 2013)* conform to American *(ASTM, 2024)* and European *(EN, 2022)* standards.

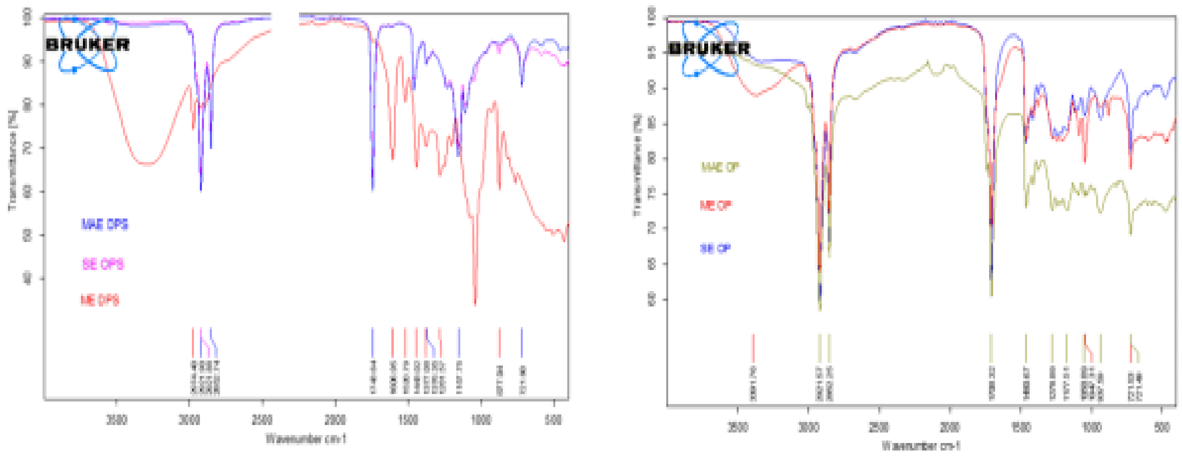

Fig 3. The FTIR spectra of: (left) DPS lipids, (right) OP lipids.

3.3 FTIR analysis

Fig. 3 (left) shows the FTIR spectrum of the DPS extracted by MAE, SE, and ME. The spectrum for the SE and MAE methods appear identical as the functional groups identified from FTIR spectrum of the oil. The peaks centred at 2921.90 cm^{-1} and 2852.74 cm^{-1} are assigned to the stretching vibrations of aliphatic C–H in CH_2 and terminal CH_3 groups. The peak at 1743.64 cm^{-1} is owing to the C=O stretching vibration of carboxylic acids of the ester. Symmetric HCH bending at 1376.35 cm^{-1} and CH_2 scissoring at 1462.24 cm^{-1}. Regarding the maceration method a large peak appears at 3299.58.cm^{-1} owing to the presence of hydrogen bonds on alcohol or phenols functions.

For the FTIR spectra of OP lipids, Fig. 3 (right), peaks at 3003.27 cm^{-1} and 2852.25 cm^{-1} corresponding to stretching vibrations of aliphatic C-H in CH_2 and terminal CH_3 groups for MAE and SE. The peak at 1708.32 cm^{-1} assigned to the C=O stretching vibration of carboxylic acids of the ester. Regarding the maceration method the peaks centred at 3430.21 cm^{-1} corresponding to the bending and stretching vibration of hydrogen bonds on alcohol or phenols functions. In the case of this raw material the similarity in number and wavenumber of peaks is clear for ME and SE lipids. Some differences appear for 721−1480 cm^{-1}.

Between DPS and OP lipids the differences can be more significant when using ME and consist of the presence of the following peaks in the DPS FTIR spectra, 1600 cm^{-1} assigned to C=C stretching of Alkenes and 1520 cm^{-1} owing to aromatic compounds stretching.

It should also be noted that the presence of oxygenated groups is intense in DPS-derived lipids.

4. CONCLUSION

OP and date palm seeds are two cheaper and available raw materials that can be valued for the production of biodiesel in Algeria. The results of lipid extraction with MAE showed that this technology is promising, especially in terms of extraction time, which was 1/6 and 2/3 of SE and ME extraction time respectively.

In contrast to the raw material and the extraction method, FTIR analyses show differences in the oxygenated compounds in the extracted lipids.

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