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Bioprospecting for seed oils from wild plants in the Mediterranean Basin for biodiesel production

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A B S T R A C T

In the Mediterranean Basin, petroleum energy resources are scarce. For an environmentally sustainable solution, the seeds collected from wild plants indigenous to this area could be used as biodiesel producers to meet the energy demand. For this, the fatty acid profiles of seed oils from 127 species belonging to 30 plant families, all native of the Mediterranean Basin, were surveyed in a search for fossil-fuel substitutes. The saponification number (SN, mg KOH/g), iodine value (IV, g I_2/100 g), cetane number (Φ), higher heating value (δ, MJ/kg), cold filter-plugging point (CFPP, °C), density (ρ, g/cm^3), induction period (IP, h) and kinematic viscosity (η, mm^2/s) were empirically determined and then used to establish the suitability of the different seed oils for biodiesel production. The aptness to serve as biodiesel was determined by applying the specification for biodiesel standard made by several organizations. In addition to three already well-characterized species, the fatty acid methyl esters from the seeds of *Conium maculatum* ($\Phi = 53.7$; $\delta = 40.1$), *Eryngium maritimum* ($\Phi = 53.2$; $\delta = 40.2$), *Nigella damascena* ($\Phi = 58.1$; $\delta = 40.1$), *Portulaca oleracea* ($\Phi = 62.9$; $\delta = 40.5$), *Prangos uechtritzii* ($\Phi = 52.8$; $\delta = 40.1$), and *Tribulus terrestris* ($\Phi = 59.4$; $\delta = 40.1$), meet the major quality standards set by several organizations, and thus are suitable for biodiesel production. Data from empirical models used for estimating biodiesel properties was compared with experimental data from biodiesel prepared with available seeds, and good correlations between the two methodologies were found.

The sowing of selected species in natural habitats, in addition to providing a valuable resource, i.e. biodiesel, both the Mediterranean Basin ecoregions and unproductive agricultural lands could be improved as appropriate habitats for wildlife, and in parallel this action would create employment in rural areas using natural resources.

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1. Introduction

Energy use makes otherwise hostile habitats adaptable to humans, for instance by powering heating and cooling systems (De Cian and Ian, 2016). Thus, expected changes in climatic conditions will increase the global demand for energy, especially in areas with an endemic energy deficiency, as occurs in the Mediterranean Basin.

The lands bordering the Mediterranean Sea in Southern Europe, North Africa, and Western Asia comprise the Mediterranean Basin ecoregions, which together constitute the world's largest and most diverse climate region, with generally mild, rainy winters and hot, dry summers (Bailey, 1998). In this area, plant communities are highly diverse, stable, and productive over the long-term, as well as strongly resilient to disturbance, and resistant to invasion by exotic species (Lavorel, 1999). Nevertheless, in some cases, native species richness shows significant declines, for example in shrub lands, old fields and dune vegetation (Gaertner et al., 2009).

The biomass produced in this area could occupy a prominent place in the future to meet energy demands. However, unless measures are taken to adapt cultivation to climate change, all bioenergy crops in Southern Europe are predicted to be severely reduced in the future. That is, the Mediterranean oilseed and solid

Abbreviations: AAS, average absolute deviation; CFPP, cold filter-plugging point; FA, fatty acid; FAME, FA methyl esters; IP, induction period; IV, iodine value; SN, saponification number; SOFA, seed oil fatty acids; wt, weight; Fcy, cetane number; η, kinematic viscosity; ρ, density; δ, higher heating value.

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biofuel crops, currently restricted to Southern Europe, are predicted to extend further north with time, generally due to higher summer temperatures (Tuck et al., 2006).

The current research on bio-energy production in the Mediterranean Basin is quite varied, highlighting the potential of several possibilities: bioethanol fuel production based on lignocellulosic residues from cereal crops, olive trees, and tomato and grape (Faraco and Hadar, 2011); *Cynara cardunculus* (Spanish thistle artichoke) to produce lignocellulosic biomass and oil seeds (Grammelis et al., 2008; Fernández et al., 2006); olive pomace oil as non-edible by-product to produce biodiesel (Che et al., 2012); liquids similar to petroleum produced from olive debris by pyrolysis (Pütün et al., 2005); pyrolysis, gasification and combustion, as a potential agricultural and animal waste exploitation method, to be utilized as a source for renewable energy (Skoulou and Zabaniotou, 2007).

Research on biodiesel in the Mediterranean Basin is timely, since the use of renewable energy is projected to increase substantially in the European Union to reach a 20% share in final energy consumption and 10% renewable energy in transport by 2020. The renewable energy contribution is further expected to increase to 55–75% of gross final energy consumption by 2050. According to the latest reports, the European Union has made significant progress since 2005 and is on track to reach its 2020 renewable energy targets (Scarlat et al., 2015).

Among the resources available in this area, wild plants could constitute a suitable alternative to produce clean energy (Guil-Guerrero et al., 2014a). Besides being directly collected in the field, seeds of different species could be sown after the selection of the most appropriate ones based on their fatty acid (FA) composition. These can be easily transformed into FA methyl esters (FAMEs), the biodiesel component, which constitutes a suitable option to replace or complement conventional fuels (Aransiola et al., 2014; Fernández et al., 2006).

Today, biodiesel is usually made from conventionally grown edible oils such as those from rapeseed, soybean, sunflower, and palm, thus diminishing food availability in exchange for fuel production (Balat, 2011). Hence, the search for non-edible plant oils as new sources for biodiesel production is needed (Chhetri et al., 2008). However, until now this research has remained marginal, and the research carried out on this topic includes a major search of weed seeds for biodiesel production in India (Azam et al., 2005), as well as the screening for halophyte species as potential biodiesel sources (Abideen et al., 2015). The ecoregions of the Mediterranean Basin constitute an ideal setting to undertake a comprehensive examination of this subject, since the area has a great variety of herbaceous plants and shrubs which have rapid growth as well as high productivity and which produce seed oils that remain unevaluated as raw material for biodiesel production.

Biodiesel has many environmental advantages, being a renewable and biodegradable alternative to conventional fuels, since it produces reduced exhaust emissions with the exception of nitrogen oxides (NOx), offering safer handling and storage, as well as more complete combustion than fossil fuels (Singh and Singh, 2010; Vasudevan and Briggs, 2008). FAMEs derived from seed oils have major properties to encourage their possible use as biodiesel fuels, i.e. saponification number (*SN*), iodine value (*IV*), cold filter-plugging point (*CFPP*), induction period (*IP*, oxidation stability), cetane number (ϕ), kinematic viscosity (η), density (ρ), and higher heating value (δ). Such features govern fuel quality, and are needed as input data to project engine combustion patterns (Ramírez-Verduzco et al., 2012). All these properties can be calculated empirically and thus used to establish the suitability of the different seed oils for biodiesel production, in the light of the specifications for biodiesel standards made by different organizations (Kalayasiri et al., 1996; Demirbas, 2008).

Although there has been a notable effort in the Mediterranean area to produce biodiesel from seeds of cultivated plants, there are no studies available on the potential use of seed oils from wild species for this purpose. In this context, the aim of the present study was to contribute knowledge concerning the potential of seed oils in the Mediterranean Basin to produce alternative fuels in an effort to diminish the endemic lack of energy resources in this area. Specifically, this study provides: i) data compilation on the FA composition of seeds from several wild species from the Mediterranean Basin; ii) experimental and empirical data for the different seed oils indicating the more prominent biodiesel quality parameters; iii) a quality assessment of the different oilseeds in the light of the various biodiesel standards made by different organizations, to discern the possible use of the different seed oils to produce biodiesel; iv) an evaluation of the empirical methods to gather data on the biodiesel quality parameters, through the use of appropriate statistical tools.

2. Material and methods

A review of several internet databases, such as are ISI Web of Science, Google Scholar, SCOPUS, and SOFA (Seed Oil Fatty Acids), was conducted to identify literature related to the FA composition of seed oils from the Mediterranean Basin. Searches were also made for biodiesels, including those from seeds of wild plants and others from cultivated plants. The keywords used individually or in combination were: fatty acid, fatty acid profile, seed, seed oil, occurrence, oleic, Mediterranean, cetane number, biodiesel, etc.

2.1. Empirical determination of quality indices for biodiesel production

2.1.1. Saponification number and iodine value

These were calculated from FAME composition of oils with the help of Eqs. (1) and (2), respectively:

$$SN = \sum (560 \cdot Ai) / MWi \tag{1}$$

$$IV = \sum (254 \cdot D \cdot Ai) / MWi \tag{2}$$

where, Ai is the FA percentage, D is the number of double bonds, and MWi is the molecular mass of each component (Kalayasiri et al., 1996).

2.1.2. Cold filter-plugging point:

This was calculated as detailed in Eqs. (3) and (4):

$$CFPP = 3.1417 \cdot LCSF - 16.477 \tag{3}$$

$$LCSF = 0.05 \cdot C14\,(wt.\%) + 0.1 \cdot C16\,(wt\%) + 0.25 \cdot C17\,(wt\%) + 0.5 \cdot C18\,(wt\%) + 1 \times C20\,(wt\%) + 1.5 \cdot C22\,(wt\%) \tag{4}$$

where CFPP is the cold filter-plugging point, LCSF is the long-chain saturated factor, and C14, C16, C17, C18, C20, and C22 are the amount of long-chain saturated FAs (LCSFAs) (wt.%) present in each oil. A minor change was made to the calculated LCSFAs compared to the previously proposed model (Ramos et al., 2009; Górnaś and Rudzińska, 2016); that is, the carbon-14 atom was included, which was omitted in the initially proposed equation due to its low influence on the potential biodiesel feedstock.

Induction period (oxidation stability)

$$IP = (117.9295/X) + 2.5905 \tag{5}$$

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