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Suitability of *Carthamus oxyacantha* plant as biodiesel feedstock

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Abstract

In this study, *Carthamus oxyacantha* (the wild species of safflower), which grows naturally without any cost and care by the time it is harvested, and is resistant to dry climate and other hard environmental conditions, is analyzed and investigated as a proper feedstock in producing biodiesel for the first time. In order to prove its suitability, its seed and oil were experimented first. The results of the experiment showed that the yield of its seed was 833-939 (kg/ha) and the amount of its oil was 24-32 %. Other properties of its oil, such as its saponification value, iodine value, and the amount of its free fatty acid content were 183, 145, and 0.18, respectively. Eventually, the methyl ester of its crude oil, which was produced through alkali transesterification reaction with methanol alcohol and NaOH as catalyst was experimented and its physicochemical properties were determined. All of the determined characteristics, namely, density (0.8816 g/ml), kinematic viscosity (4.13 mm^2/s at 40 ºC), flash point (179 ºC), cloud point (-3 ºC), pour point (-9 ºC), sulfur content (0.01 mass %), carbon residue (0.005 mass %), vacuum distillation end point (352 ºC at 90% volume recycle), gross calorific value 39.255 (Mj/Kg) and calculated cetane index (48.99) meet the two accepted biodiesel standards (i.e. ASTM D6751 and EN 142140). Therefore, according to the results, *Carthamus oxyacantha* plant, which was not reported earlier, can be utilized as a possible biodiesel feedstock.

Keywords: Alkali transesterification; Methyl ester; Oilseed; Raw material; Alternative fuel.
Abbreviations: ASTM- American Society for testing and materials; EN- European norm; CP- Cloud point; PP- Pour point; PM- Particulate Matter; PAH- Poly aromatic hydrocarbons; So_{x-} Sulphur oxides; EU- European Union; FFA- Free fatty acids.

Introduction

The depleting reserves of fossil fuels, increasing demands for diesels and uncertainty in their availability, global warming due to emission of green house gases and environmental pollution are the major key factors leading to the search for alternative sources of energy. Water, solar, wind and biofuel are the most notable alternative sources of energy (Singh and Singh, 2010; Atadashi et al., 2011).The use of biofuels produced through the transesterification of vegetable oils with alcohols is currently considered to be feasible energy option (Yanez Angarita et al., 2009). Two global liquid biofuels are biodiesel and bioethanol. Biodiesel is typically produced via transesterification reaction, by reacting a vegetable oil or animal fat with alcohol (methanol or ethanol) in the presence of a catalyst (NaOH, KOH, or alkoxides) to yield methyl or ethyl esters (biodiesel) and glycerin (Demirbas, 2011; Demirbas, 2009). Biodiesel can be used as a basis for a clean substitute for fossil fuel without any modification in diesel engines, boilers or other combustion equipment. Previous studies have shown that biodiesel produces substantially less CO, CO_2, particulate matter (PM), poly-aromatic hydrocarbons (PAH), Sulfur oxides (SO_x) and HC emissions than fossil fuels. A life cycle analysis of biodiesel showed that overall CO_2 emissions were reduced by 78%, compared with petroleum-based diesel fuel (Soloua et al., 2010). The raw material costs and limited availability of vegetable oil feedstocks are always critical issues for the biodiesel production. The high cost of vegetable oil, has led to the production cost of biodiesel becoming approximately 1.5 times higher than that for diesel (Phan and Phan, 2008). Currently, more than 95% of the world biodiesel is produced from edible oils (Balat, 2011). By converting edible oils into biodiesel, a lot of problems may arise; global imbalance to the food supply and demand market, deforestation, and destruction of ecosystems. For instance a 5% displacement of diesel in the USA requires about 13% of available cropland to produce biodiesel; while in the EU 15% is required. In other words, arable land that would, otherwise, have been used to grow food would, instead, be used to grow fuel (Demibas, 2008). In order to overcome these problems it is important to introduce new plants with low costs, high oil yield, and proper oil composition, which grow in the marginal and waste lands. *Carthamus oxyacantha*, as one of the annual wild species of safflower, is widespread in Turkey, subtropical regions of western Iraq, Iran, northwest India, Kazakhstan, Turkmenistan, and Uzbekistan. This species is important because it is assumed to be the ancient male parent of cultivated safflower. It is resistant to saline conditions, water stress and can reach the deep-laying water (Sabzalian et al., 2008; Dordas and Siloulas, 2009). In addition, it has no production cost prior to the harvesting operation. To maintain the sustainable biodiesel production, the collection of scientific data on oilseeds yield, oil content and the quality of the raw materials is required. A few researchers have reported the fatty acid composition of *Carthamus oxyacantha* oil. According to Sabzalian et al. (2008), oil content of *Carthamus oxyacantha* is 25.34 ± 2.98% and its oil composition consists of 7.28 ± 0.55, 3.16 ± 0.60, 17.08 ± 1.37 and 70.61 ± 2.27%, palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) acids, respectively. Carpetian and Zarei (2005), also found that the *Carthamus oxyacantha* oil had a high percentage of unsaturated fatty acids (≥ 80%). Studies about this plant (yield and other seed characteristics) and its oil characteristics are limited. No literature is available on the assessment of this wild plant suitability as biodiesel feedstock. A lower cost biodiesel feedstock is desirable, provided that the quality of the methyl ester extracted from it reaches an acceptable standard. The aim of this work is to evaluate the suitability of this plant as biodiesel feedstock.

Results and discussion

The properties of *Carthamus oxyacantha* seed, extracted oil, and derived methyl ester have been tested to evaluate the suitability of this plant as a biodiesel feedstock.

Seed characteristics

The seed properties of *Carthamus oxyacantha* are shown in Table 1. The results showed that, the weight of 1000 seeds of *Carthamus oxyacantha* and seed yield were 16-20 (g) and 833-937 (kg/ha), respectively. The seed oil content was 24-32 (%), and the oil yield value of it was 200-300 (kg/ha). Its lower oil yield can, partly, be compensated for, since the plant is wild and has no costs prior to the harvesting operation. The seeds color was brown with black strips, as shown in Fig 1.

Crude oil properties

Some oil properties, namely free fatty acid, iodine value and saponification value were determined via standard methods that were mentioned in the previous section. The tests were repeated three times and the results have been reported as a mean in Table 2. As shown in Table 2, the saponification value (the milligrams of potassium hydroxide required to saponify 1 gram of the oil) of *Carthamus oxyacantha* oil was 183. Iodine value is the measure of unsaturation of oils and fats, and it is expressed in centigrams of iodine absorbed per gram of oil (Wan, 2000). As shown in Table 2, the *Carthamus oxyacantha* oil iodine value was 145. This high amount confirmed the high percentage of unsaturated fatty acids in *carthamus oxyacantha* oil, which was found by former studies (Sabzalian et al., 2008; Carpetian and Zarei, 2005). Free fatty acid (FFA) content is the amount of fatty acid (% wt) in the oil which is not attached to triglyceride molecule (Karmakar et al., 2010). As seen in Table 2, the free fatty acid content of the *carthamus oxyacantha* oil was 0.18; therefore, the alkali catalytic transesterification method was applied.

Table 1. Seed properties of *Carthamus oxyacantha* .

Property	Values
1000 seed weight (g)	16-20
Oil content (%)	24-32
Seed yield (kg/ha)	833-937
Oil yield (kg/ha)	200-300
Colour	Brown with black strips

Fig 1. Seeds of *Carthamus oxyacantha* plant.

Fuel properties

The physicochemical properties of produced methyl ester were determined by ASTM standard methods in triplicate and mean values were compared to ASTM D6751 and EN 14214, the two accepted biodiesel specification standards (Table 3). Density is the mass per unit volume of any liquid at a given temperature. It has importance in diesel-engine performance, since fuel injection operates on a volume metering system (Demirbas, 2008). It can be found in Table 3 that the density of *Carthamus oxyacantha* methyl ester (0.8816 g/ml) is within the EN 14214 standard range (0.86-0.9 g/ml), and ASTM D6751 has no range for density. Viscosity is a key fuel property because it influences the atomization of a fuel, upon injection into a combustion chamber, and eventually the formation of the soot and engine deposits (Rashid et al., 2009; Konthe, 2005). The conversion of triglycerides into methyl or ethyl ester through the transesterification process, reduces the molecular weight by one-third that of the triglyceride and also reduces the viscosity by a factor of about eight and increases the volatility, marginally (Singh and Singh, 2010). The determined kinematic viscosity of *carthamus oxyacantha* methyl ester, as shown in Table 3, was 4.13 mm^2/s at 40 ºC. The obtained value satisfied both ASTM D6751 (1.9- 6.0 mm^2/s) and EN 14214 (3.5-5.0 mm^2/s) standards requirements. The flash point is the lowest temperature at which a combustible mixture can be formed above the liquid fuel (Van Gerpen et al., 2004). For safe handling and storage, a proper flash point is required. Number 1 and 2 diesel fuels are required to have flash point above 38 ºC and 52 ºC, respectively. Biodiesel has a high flash point; usually more than 150 ºC. If methanol, with its flash point of 12 ºC, is present in the biodiesel, the flash point can be lowered, considerably (Van Gerpen et al., 2004). According to ASTM D6751 and EN 14214 standards, biodiesel must have minimum values of 130 ºC and 120 ºC, respectively.

Table 2. Chemical properties of crude *Carthamus oxyacantha* oil

Property	Values	Test method	Reference
Free fatty acid (%)	0.18	AOCS (Ca 5a-40)	AOCS, 1998
Iodine value (g I/100g)	183	AOCS (Cd 1-25)	AOCS, 1998
Saponification value (mg KOH/g)	145	AOCS (Cd 3-25)	AOCS, 1998

The determined flash point of *Carthamus oxyacantha* methyl ester meets these requirements, and was 179 ºC (Table 3). The cold flow properties, basically, concern the changes of biodiesel properties such as crystallization, gelling or viscosity increase due to temperature changes that might adversely affect the operability of the vehicles. These properties are reflected by the values of cloud point (CP) and pour point (PP), and will be the determining factor of whether or not the produced biodiesel can be used in cold climate countries. In addition, these properties are determined by types of fatty acids in the feedstock oil (Gui et al., 2008). For example, biodiesel fuels derived from palm oil and beef tallow have poor cold flow properties, because they have a high content of saturated fatty acids (Gui et al., 2008; Ma et al., 1999). In this study CP and PP of produced fuel were -3 ºC and -9 ºC, respectively. As reported earlier (Sabzalian et al., 2008; Carpetian and Zarei, 2005), *Carthamus oxyacantha* oil has a low content of saturated fatty acids; therefore, low values of CP and PP are due to this low content of saturated fatty acids. Sulfur content and carbon residue of *Carthamus oxyacantha* methyl ester were found to be 0.01 (mass %) and 0.005 (mass %), respectively (Table3). Both of these characteristics meet the specification requirements of ASTM D6751 and EN 14214 standards. The maximum allowable vacuum distillation end point of biodiesel (at 90% volume recycle), according to the ASTM D6751, is 360 ºC. As seen in Table 3, the produced methyl ester, with 352 ºC distillation end point (at 90% volume recycle), was satisfactory, according to this requirement. The determined gross calorific value (higher heating value) of *carthamus oxyacantha* methyl ester was 39.255 (MJ/kg). There is no specification requirement for the gross calorific value in biodiesel standards. As illustrated in Table 3, the calculated cetane index of produced fuel (48.99) meets the minimum cetane number requirement (47) in ASTM D6751, but is lower than that of EN 14214.

Material and methods

Plant material

30 kg of *Carthamus oxyacantha* seeds were collected from Sanandaj region (Kurdistan province). Then the collected seeds were transferred to a laboratory for subsequent experiments. Oil extraction, oil characteristics determination, and methyl ester production were carried out in the Research Laboratory of Agriculture Faculty of Sanandaj Azad University, and methyl ester characterization was performed at Research Institute of Petroleum Industry, Kermanshah Campus. All chemicals used in this work were of analytical reagent grade and were used without further purification.

Determination of Carthamus oxyacantha seed characteristics

After determining the seeds' color, they were dried at 40 ºC for 4 hours, using an oven, with constant moisture content. Then the weight of 1000 seeds (g) was determined by weighing. To determine the oil content (%), the dried seeds were ground by a grinder, and the oil content was measured through soxhlet extraction method by n- hexane solvent (IBPGR, 1983; Bozan and Tamelli, 2008; AOCS, 1998). By using the oil content and seed yield, oil yield was calculated:

$$OY = OC \times SY \quad (1)$$

$$SY = \frac{10000\ m^2 \times CS}{A}, \quad (2)$$

where:

OY = Oil yield (kg/ha)
OC = Oil content (%)
SY = Seed yield (kg/ha)
CS = Collected seeds (kg) from a plot
A = Area of plots (m^2)

Oil extraction

In order to carry out the oil extraction process, the dried and ground seeds of *Carthamus oxyacantha* were fed into a soxhlet extractor fitted with a round bottom flask. The extraction was performed on a water bath for 5 hours with n-hexane. The solvent was removed at 40 ºC, under vacuum, using a rotary evaporator (Bozan and Tamelli, 2008).

Oil properties determination

Some properties of crude *Carthamus oxyacantha* oil namely, free fatty acid, iodine value and saponification value were determined according to the AOCS (Ca 5a-40), AOCS (Cd 1d-92) and AOCS (Cd 3-25) methods, respectively (AOCS, 1998).

Transesterification

Since the crude *Carthamus oxyacantha* oil had free fatty acid content less than 0.5%, the alkali transesterification method was chosen. Prior to the transesterification, the crude oil was kept in an oven at 105 ºC for 2-3 hours to remove water from it, and sodium hydroxide pellets were then dissolved in methanol by stirring to prepare a sodium hydroxide-methanol mixture. The reaction was carried out in the following conditions: oil to methanol molar ratio (1:6), catalyst concentration (1w/wt%), reaction temperature (60-65 ºC), ambient pressure, reaction time (1h) and stirring speed 400 rpm. The preheated crude oil was poured into a 1 liter round bottom flask which was fitted with a thermometer and condenser. Then the NaOH- methanol mixture was added into the oil flask, and was continuously stirred to 400 rpm by means of magnetic stirrer for 1 h. Then, the mixture was transferred into a separating funnel, and was allowed to settle under gravity for 20 h. Two liquid phases were produced; the upper phase was methyl ester (biodiesel) and the lower was crude glycerin. The glycerin was drained out, and methyl ester was washed with warm deionized water. Finally, the product was heated and dried (Ikwuagwu et al., 2000; Keera et al., 2011; Venkanna and Venkataramana, 2009; Demirbas, 2008; Konthe, 2010; Freedom et al., 1984).

Table 3. The physicochemical properties of *Carthamus oxyacantha* methyl ester in comparison with ASTM D6751 and EN 14214 (Biodiesel specification standards)

Property	Carthmus oxyacantha methyl ester (this study)	ASTM D6751 (ASTM, 2007)	EN 14214 (EN14214, 2003)
Density (g/ml)	0.8816	-	0.86-0.90
Kinematic viscosity (mm^2/ s at 40 ºC)	4.13	1.9- 6.0	3.5-5.0
Flash point (ºC)	179	130 min	120 min
Cloud point(CP) (ºC)	-3	Report	-
Pour point (PP) (ºC)	-9	-	-
Sulfur content (mass %)	0.01	0.05 max	0.1 max
Carbon residue (mass %)	0.005	0.05	-
Vacuum distillation end point (ºC)	352 (at 90% volume recycle)	360	-
Gross calorific value (Mj/kg)	39.255	-	-
Calculated cetane index	48.99	47 min	51 min

Characterization of Carthamus oxyacantha methyl ester

Methyl ester density [ASTM D4052] at 15 ºC, kinematic viscosity [ASTM D445] at 40 ºC, flash point [ASTM D93] and sulfur content [ASTM D2622], were measured by using density meter (Model DMA48, Austria), Ostwald viscometer, K16200 Pensky-Martens closed cup flash point tester and X-Ray Fluorescence Spectrometer (SLFA-1100 H model, Horiba Instruments, Inc), respectively. Cloud point (CP), Pour point (PP), carbon residue and distillation limit of methyl ester were determined, according to the ASTM D2500, ASTM D97, ASTM D189, and ASTM D1160 standards, respectively. Determination of gross calorific value (higher heating value) was determined according to the ASTM D240 by using IKA Calorimeter System C4000, Adiabatic (ASTM, 2007). The cetane index was calculated according to the ASTM D976 empirical equation (Van Gerpen et al., 2004);

$$CI = 454.74 - 1641.416D + 774.4D^2 - 0.554T_{50} + 97.803 \times [\log_{10}(T_{50})]^2 \quad (3)$$

where,

D = fuel density at 15°C in g/ml.

T_{50} = the temperature corresponding to the 50% point on the distillation curve in degrees C.

Conclusion

An annual wild plant, *Carthamus oxyacantha* not reported earlier, has been evaluated for biodiesel production. From the results of this study it was found that the oil content and seed yield of *Carthamus oxyacantha* seed were 24-32 (%) and 833-937 (kg/ha), respectively, and also some crude oil characteristics, such as saponification value, iodine value and free fatty acids content (FFA) were 183, 145 and 0.18, respectively. Methyl ester (biodiesel) of crude carthamus oxyacantha oil was produced by alkaline transesterification. All the determined characteristics of the produced biodiesel meet the two accepted biodiesel standards (i.e. ASTM D6751 and EN 14214) specification requirements. Therefore, according to the obtained results from this study, carthamus oxyacantha plant can be considered as a biodiesel feedstock.

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