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Biodiesel production by transesterification of *Acacia raddiana* seed oils

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ABSTRACT

Oil was obtained from the seed of *Acacia raddiana* with 11% yield , allowing the possibility of economical exploitation, and its fatty acid composition was determined by gas chromatography. The crude oil was transesterified using acid and base catalysts (H_2SO_4, HCl, NaOH, C_2H_5ONa), with a molar ratio of Methanol: Oil: Catalyst of 5: 1: 0.1, to form biodiesel. The physicochemical properties of the fatty acid methyl esters (FAMEs) formed are in agreement with the biodiesel, making it a potential candidate to be an alternative biofuel.

KEYWORDS

Acacia raddiana;
Biodiesel;
Transesterification;
Seed oils;
Environement.

INTRODUCTION

The major part of all energy consumed worldwide comes from petroleum as largest single source, exceeding charcoal, natural gas, hydro, nuclear. However, these sources are limited, and will be exhausted[1]. Looking for alternative sources of energy is of vital importance, thus renewable energy sources are developed worldwide, owing to high oil prices and to limit greenhouse gas emissions. Vegetable oils are a renewable and potentially inexhaustible source of energy, non-toxic, biodegradable in water, contains less sulfur compounds and has a high flash point (>130°C). Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines[2,3].

Due to their high viscosity and low volatility, the direct use of vegetable oils in fuel engines is problematic, they do not burn completely and form deposits in the fuel injector of diesel engines, and formation of toxic acrolein. Different ways have been considered to reduce the high viscosity of vegetable oils: Dilution of vegetable oil with diesel fuel; Microemulsions with short chain alcohols; Thermal decomposition; Catalytic cracking; Transesterification with ethanol or methanol[3-6]. Among all these alternatives, the transesterification seems to be the best choice, as the process is relatively simple and the characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel[7]. Several vegetable oils, with a diversified composition in fatty acids, are studied for the preparation of biodiesel: Castor, cottonseed[8], jatropha[9], palm[10], pongamia[11], rapeseed[12], rubber[13], soybean[4-7], sunflower[14] and virgin[15] oils.

To the best of our knowledge, there are no references about the oil composition and biofuel production from *Acacia raddiana*. Thus, in continuation of our effort on the valorisation of Algerian Sahara plants as biomaterials[16,17], We report herein our results in the studie of biodiesl production from the seed of the Saharan tree: *A. raddiana*.

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EXPERIMENTAL

Plant material

The genus *Acacia* (Family Fabaceae; subfamily Mimosoideae) is a cosmopolitan tree of dry areas containing in excess of 1350 species[18]. In Algerian Sahara, the specie *Acacia raddiana* (local name : Talh), is known for its multipurpose benefits and used as folk medicinal plant for the treatment of various diseases (pulmonary diseases, occular affections, jaundice and antidiarrhoeic), provide food and shelter for many desert animals and are a major source of livestock feed and firewood for the native people[17b,19].

Seed of tree *Acacia raddiana* used in this work was collected from Saoura desert (Bechar, Algeria) in August 2008. The biomass was washed with distilled water several times to remove soil-associated particles and water soluble materials.

Oil extraction

The oil was extracted from 300 g powdered seeds with n-Hexane by the continuous technique in a Soxhlet extractor for 10 h, after that, the hexane fraction was dried with Na_2SO_4 and the solvent was removed under reduced pressure in a rotary evaporator, the oil extract was weighed and the results were expressed as a percentage of dry seed. The composition of the oil with regard to fatty acid content was determined by gas chromatography analysis (GC).

GC analysis

The n-Hexane extract of *Acacia raddiana* seed was analyzed by analytical gas chromatography using a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector. 1 μL of the oil extract was injected in split less mode onto a Supelco CBP-5 capillary column (30 m. 0.25 mm, film thickness 0.25 μm). The oven temperature was programmed as follows: 60°C for 2 min, then rising to 240°C at 3°C/min, then to 300°C for 10°C/min, ending with 10 min at 300°C; carrier gas, He at a flow rate of 1.0 ml/min; injector and detector temperature, 250°C. Fatty acids were identified by comparison of their retention indices (Determined relative to the retention times of a n-alkanes homologous series).

Properties of seed oil

Physico-chemical properties of *Acacia raddiana* seed oil and its fatty acid methyl esters (biodiesel) formed viz; colour, refractive index (at 28°C), acid value, iodine value, density (at 28°C), kinematic viscosity (at 40°C) and calorific value were determined in accordance with the AOAC and ASTM standard procedures[20,21]. All data reported here are arithmetic means of triplicate assays.

Transesterification reactions

All chemical reagents used in this study were of commercial grade and used without further purification. Anhydrous methanol was stored over $MgSO_4$ as desiccant.

Transesterification reactions were carried out in a 100 mL three-necked glass flask equipped with a reflux condenser and a thermometer under magnetic agitation. The reaction mixture containing Methanol, Oil and the Catalyst (H_2SO_4, HCl, NaOH or C_2H_5ONa), with a molar ratio respectively 5: 1: 0.1, was allowed to alcohol reflux for a time period of 1, 2, 3 and 4 h, after which the alcohol was recovered by distillation. The formed mixture was neutralized with aqueous solution of $NaHCO_3$ (5%) or H_3PO_4 (5%), respectively in case of acid or basic catalysts and washed three times with distilled water. The organic phase was separeted in separatory funnel and dried in the presence of $MgSO_4$. The biodiesel yield was determined by gas chromatography and expressed in terms of the percentage (wt%) fatty acid methyl esters (FAMEs) formed according to the described procedures[22].

RESULTS AND DISCUSSION

Fatty acid profile of the *Acacia raddiana* seed oils

Oil was obtained from the seed of *Acacia raddiana* with 11% yield, was generally considerably higher that those found in the seed of *Acacia nilotica*[23] and the wood of other *Acacia* species (*A. longifolia*, *A. dealbata*, *A. Melanoxylon* and *A. retinodes*)[24], allowing the possibility of economical exploitation.

TABLE 1, present the fatty acid profile for n-Hexane extract of seed oil from *A. Raddiana* determined by GC, the following fatty acids were identified: palmitic,

TABLE 1 : Fatty acid composition of *Acacia raddiana* seed oils

Fatty Acid	Carbon Chain	Content (%)
Palmitic	C16:0	38.3
Stearic	C18:0	6
Oleic	C18:1	34
Linoleic	C18:2	21
Unidentified	-	0.5
Saturated fatty acid	-	44.3
Unsaturated fatty acid	-	55

TABLE 2 : Yield of FAMEs in the methanolysis of *Acacia raddiana* seed oils

Catalysis	Reaction time (h)			
	01	02	03	04
	FAMEs Yield (%)			
H_2SO_4	5	5	8	13
HCl	4	5	6	10
NaOH	63	90	90	92
C_2H_5ONa	88	88	80	92

stearic, oleic and linoleic acids. The main fatty acid found in the *A. raddiana* seed oil was palmitic acid followed by oleic acid. The total saturated and unsaturated fatty acid composition was 44.3% and 55%, respectively. The major saturated acid present in this oil was palmitic acid (38.3%) and stearic acid with less concentration (6%). Two unsaturated fatty acid were found oleic acid (34%) followed by linoleic acid (21%).

Transesterification of the *Acacia raddiana* seed oils under acid and basic catalysts

Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous catalysts. The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction[25]. It has been reported that, if free fatty acid (FFA) content in the oil were about 3%, the reaction is not suitable to produce oil esters[13]. However, homogeneous acid catalyzed reaction is not strongly affected by the presence of FFAs in the feedstock. In fact, the reaction can simultaneously catalyze both esterification and transesterification and is about 4000 times slower than the homogeneous alkali-catalyzed transesterification[26]. The problems associated with the homogeneous catalysts are the formation of unwanted soap byproduct by reaction of the FFA, generation of wastewater during separation and cleaning[27].

TABLE 2, present the production (percentage yield) of fatty acid methyl esters (FAMEs) by the methanolysis of *A.raddiana* seed oils in the presence of conventional homogeneous catalysts (H_2SO_4, HCl, NaOH or C_2H_5ONa) for different period time. The reaction conditions were: molar proportions of MeOH: Oil: Catalyst (5: 1: 0.1) at methanol reflux with constant magnetic stirring.

The comparison between basic- and acid-catalyzed reactions indicates that basic catalysis is very much more efficient than acid catalysis. In the presence of basic catalysts an average yield of FAMEs of 92% was obtained after 04 hours of reaction, whilst with sulfuric and chlorhydric acids than 13% of ester was produced. These results are in line with those reported for other vegetable oils that exhibit typical fatty acid composition[26-29]. The use of basic alkoxide or hydroxide produced the highest yields of FAMEs (TABLE 2). The active species in both systems were the methoxide ions formed by the large excess of MeOH in the medium. The diminition of the yield of ester in the first hours of reaction when hydroxide catalysts are used, is du to the side reactions, such as hydrolysis and saponification actived by the production of water molecules[8].

Physico-chemical properties of oil and biodiesel from *Acacia raddiana* seed

The oil obtained using the non-polar organic solvents (n-Hexane) from the seed of *Acacia raddiana* was used for the determination of physico-chemical properties, important from biodiesel aspect. Some properties of oil and FAMEs (biodeisel) products were determined and are shown in TABLE 3.

In our experiment, we recorded the density to be 912 kg m^{-3} at 28°C for n-Hexane extracted seed oil of *A. raddiana*. The density of the seed oil is similar to those of the other vegetable oil, it is higher than the acceptable ranges of petroleum diesel (820-845 kg m^{-3}) as per the current ASTM requirement[21,22]. Biodiesel is considerably more susceptible to autoxidation than petrodiesel and autoxidation is a serious threat to biodiesel fuel quality. Thus, oil obtained from the seed of *A. raddiana* was characterized by lower contents of unsaturated fatty than other vegetable oils[4-10,14,22], where affects directly the oxidation stability of the

TABLE 3 : Properties of the oil and biodiesel of *Acacia raddiana*

Property	Oil	Biodiesel
Color	Amber	Amber brown
Refractive Index at 28°C	1.3975	1.3896
Acid Value	0.4	-
Iodine Value	63.32	63.10
Density (kg m^{-3} at 28 °C)	912	876
Kinematic viscosity (mm^2 s^{-1} at 40 °C)	37.4	4.1
Calorific value (MJ kg^{-1})	-	32.78

biodiesel from which it was produced. This low degree of unsaturation is expressed by the iodine value obtained for the biodiesel produced 63.10, which it is in agreement with EN 14214 specification[22]. This result indicated that such a biodiesel can present a suitable chemical stability against oxidation.

The calorific value for petrodiesel is 45.4 MJ kg^{-1} whereas those for the seed oil of *A. raddiana* extracted is 32.78 MJ kg^{-1}. This low energy content is due to the presence of chemically bound oxygen in the fatty acid chains as has been reported[27]. The viscosity is an important physical property of a liquid fuel, the kinematic viscosity values for the *A. raddiana* seed oil recorded at 40°C in our experiment is 37.4 mm^2 s^{-1}. The kinematic viscosity of the oil is in the range of those reported for other vegetable oils (30-40 mm^2 s^{-1} at 40°C) used for biodiesel production[9]. The viscosity of *A. raddiana* seed oil was reduced by transesterification, thus we recorded in our experiment at 40°C a value of 4.1 mm^2 s^{-1} for the liquide FAMEs (Biodiesel) obtained, which was in the range recommended by ASTM. The ASTM standard for biodiesel viscosity is 1.9-6.0 mm^2 s^{-1} at 40°C[21,22]. From this results it is clear that not much difference lies in the physico-chemical properties of *A. raddiana* seed oil, extracted using n-Hexane compared to other vegetable oils used for biodiesel production.

CONCLUSIONS

From the seed of the Saharan tree *Acacia raddiana*, Oil was obtained with 11% yield , and its fatty acid composition was determined by gas chromatography. A biodiesel was formed by transesterification of the crude oil by using conventional homogeneous catalysts (H_2SO_4, HCl, NaOH, C_2H_5ONa) and methanol. Based on the results obtained in this study regarding the characterization of crude oil for various physico-chemical properties demonstrated that, almost all the important properties of seed oil from *Acacia. raddiana* and its methyl esters are in agreement with the biodiesel making it a potential candidate to be an alternative economical biofuel, in view to limite supply of natural fossil fuel.

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