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Quality Study of biodiesel produced from *Ricinus communis* L. (Kharouaa) in southwest Algeria

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ABSTRACT/RESUME

Abstract: *Castor oil plant (Ricinus communis L.), as a non-comestible energy harvest, it can be utilized for different biofuels preparation. Extracted castor oil was utilized for biodiesel (BD) preparation by transesterification method, whereas the castor plant remains, including stalk, seed cake, and leaves, were used for ethanol and biogas preparation. Operating setting effects, like methanol to castor oil plant ratio, temperature, and reaction time on BD income production were examined. The best BD yield reached 91% at oil molar ratio 9:1 methanol to castor oil mass ratio obtained at 60°C during 60min. This yield corresponded To 910g BD per kg castor plant oil. According to tracking the distillation process of the obtained BD it is positive and it is located between light and heavy diesel, Also, the latter (BD) is not harmful to the environment.*

I. Introduction

The majority of energy spent in the world becomes mostly from petroleum based fuels. The quantity of the non-renewable sources is permanently decreasing. The fossil fuel crisis and energy safety becoming a common concern issues of the humanity [1]**.** Meanwhile, the climate change due to the environmental pollution and greenhouse-effect produced by great scale burning of petrochemical fuels caused by the growth of modernization and industrialization are receiving increasingly serious attentions [2, 3]. Developing sustainable and ecofriendly green energy alternative fuels have increasingly become the emphasis of governments, institutions and people. Amid them, biodiesel (BD) is reported as one of the most interesting ways to resolve the international issues of liquid energy within the last years [4].

Biodiesel (BD) has similar properties to petrodiesel; it has been reported as a competitive alternative renewable and sustainable fuel for petroleum diesel. It has numerous advantages counting; biodegradability, production less harmful gas emissions, lower pollution, higher flash point and also negligible sculpture. Biodiesel can be blended to the petrodiesel according to several rates or it can be employed as a pure fuel [4]. Several comestible and non-comestible feed stocks can be utilized for BD generation. However, availability and cost of the oil feedstock limited the BD generation. Therefore, non-comestible oil feed stocks, counting waste coming from cooking oils, lipids, non-comestible vegetable oils and animal fats [5,6] were exploited as inexpensive feed stocks for BD generation to reduce the generation cost of BD. Amongst non-comestible oils that has been more attractive as a feed stock for BD preparation is castor (*Ricinus communis*) seed oil, because to it is unsuitable for human ingesting and it doesn't contest with food crops, as well as its high content of oil of 50% and its high oil output that reaches 1200 kg-oil/ha/year. Moreover, the castor plant doesn't require a great upkeep or high quality water in addition it can be cultivated in marginal and bordering soils. Castor oil plant is considered as a good-looking and it presented a low cost feedstock for BD production [7].

Vegetable oils can be utilized as a biofuel of diesel engines whichever in its direct form but requires several engine modifications. Typically, three techniques were used to improve the properties of the neat vegetable oils and fats, counting dilution with whichever diesel fuel or solvents like micro emulsification, transesterification and pyrolysis [8]. Though, there were many of diverse techniques for BD and bio-gasoline generation. Such biofuels could be mixed with the classical fuels like diesel or gasoline to be used as solvents for improving the behavior and emissions of internal combustion engine. These properties of BDs were high oxygen and energy contents, cetane and octane indexes, low residue and zero Sulfur contents. Consequently, they were used for increasing the resistance of the irregular combustion, behavior and emissions of compression rate and spur ignition engines [9]**.**

Biodiesel is produced from vegetable oils or animal fats by substituting a glycerol group in the aliphatic chain based on short chain alcohol, which constitute an important green and bioenergy source [10]. The most used technic for BD production is Alkali catalyzed transesterification [11]. Homogeneous alkali catalysts are increasingly abandoned due to their complex treatment process inducing a large quantity of waste water, saponification, reactor corrosion and environmental pollution [12, 13].
Castor plant known scientifically as *(Ricinus communis L.)*, is poisonous plant, belongs to the family of *Euphorbiaceous* which vary in appearance, the plants of this family are essentially characterized by their white latex, irritating skin, sticky and thick; an evolution of floral morphology from classical flowers [14].

Due to the high commercial importance of the extracted oil from the castor bean (castor oil plant), it is cultivated in many country in the world. It has been found in Egyptian tombs dating back to 4000 BC; the slow burning oil was mostly used to fuel lamps [15,16]. In addition, it is reported that this plant has originated in the tropical belt of both India and Africa. Il is cultivated in 30 different countries of which India contribute by about 75% of castor beans, the remaining being produced in China 10%, Brazil 5%, Russia, Thailand, Ethiopia, Philippine and some other African countries [17, 18].

Castor is an oleaginous plant, these grains are rich in oil which is considered toxic for humans Global Invasive Species Database [19], on the other hand it can be used in various industrial sectors. This plant exists in Adrar oases in the northern of Algeria and nowadays it is scattered because of the absence of significant industrial exploitation of the oil of these grains except some uses in the traditional field. The main goal of the present research work is to study the quality of biodiesel produced from castor oil in the Adrar region based on the esterification process.

II. Materials and methods

II.1. Materials and experimental setup

Analytical grade methanol (CH_3OH) (99%), potassium hydroxide (KOH) in pellet form of above 85% purity and n-hexane (C_6H_{14}) were obtained from Prochima Sigma, were used for the biodiesel production. Ricin seeds were collected from the Ricin trees in Adrar user/ms in southern Algeria. Prior to oil extraction, the collected Ricin seeds cleaned and dried in an oven at 105°C to remove water and wast.

II.2. Soxhlet extraction

Soxhlet extraction apparatus was to extract the oil from *Recinus communis* seeds. In this experiment 300mL of n-hexane was poured into round bottom flask. 10 grams of powdered *Recinus communis* was placed in thimble and inserted in the center of the extractor. The flask was heated and when n-hexane was boiling, the vapor rises through the vertical tube into the condenser at the top. The liquid condensate drips into the filter paper thimble in the center, which contains the oil to be extracted. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This was allowed to continue for 30 minutes. At the end of the extraction, the resulting mixture containing the oil and n-hexane was distilled off using simple distillation to recover solvent from the oil. The amount of oil extracted was then weighted to determine the oil content and finally stored in a glass bottle prior to biodiesel production. The process steps to obtain of the oil extracted from castor oil plant are given by Figure 1.

Figure 1. *Castor oil operating process*

II.3. Transesterification process of castor oil

The criteria for using one or two steps transesterification process depends on the free fatty acid content (FFA). If this ratio is less than 2.5%, then one step transesterification process with a base catalyst should be used and if the FFA ratio exceeds 2.5%, two steps transesterification process should be accomplished. In the present study, the FFA content of RCO was AV= 1,148 mg KOH/g oil, then one step treatment is sufficient. The experiments were carried out by considering the temperatures 60°C, and methanol castor oil molar ratios 9:1, catalyst concentrations 1wt% of castor oil; and reaction time (60 min) [20, 21]. Oil was placed in two-necked batch reactors and heated to the required temperature. The stirrer speed was maintained at 400 rpm for constant mixing. The methoxide solution was prepared by dissolving the exactly measured quantity of solid catalyst (KOH) in premeasured quantity of methanol. Once the oil reached the required temperature, the prepared methoxide was slowly poured into the reactor. After an appropriate period of time, excess alcohol was evaporated at a mild temperature under moderate vacuum on a rotary evaporator. The mixture was transferred to a separating funnel, and then allowed to stand for phase separation. The remaining crude biodiesel produced from castor oil was gently washed with distilled water at 40°C in order to remove the unreacted methanol, catalysts and impurities, finally the washed biodiesel was dried in oven at 110°C for 30 min [15, 16]. The flowchart of biodiesel production is giving by Figure 2.

The percentage yield of studied biodiesel is calculated according to Eq.1:

$$\text{Biodiesel yield (\%): } Y = \frac{\text{Grams of methyl ester produced}}{\text{Grams of oil used in reaction}} \times 100 \qquad (1)$$

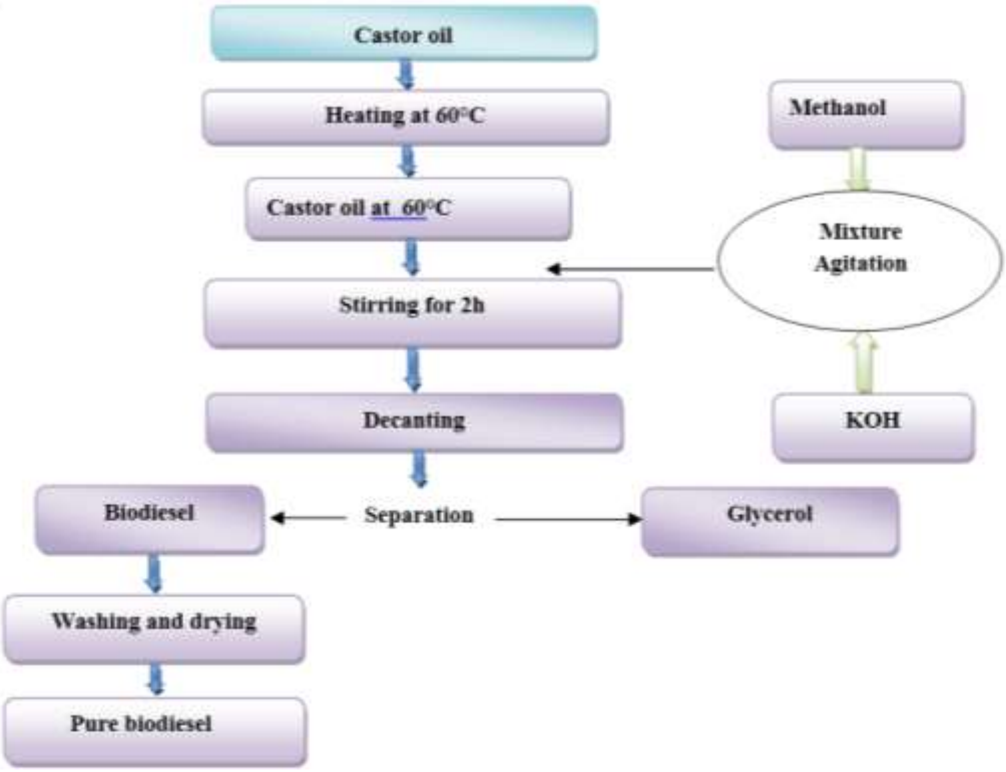

Figure 2. *Biodiesel production flowchart*

II.4. Castor oil plant seeds characterization

The castor oil plant water content is determined using NFV03-921 method and the fat content using NFENISO734-1, 2000 method, the ash content by the method AFNORV03-922 and the crude protein content was determined according to AFNORV18-100 method.

II.5. Characterization of castor oil

The density of the extracted oil from the castor oil plant is determined using AFNORT60214 method and the extracted oil refractive index is determined according to AFNORT60212 method. The European standard ISO 31040 of 1994 method is used to determine the viscosity of the extracted oil. Finally, the acid value (AV) and saponification index are determined using the methods AFNORT60204 and AFNORT60206 respectively. Iodine value was measured according to ASTM D4607 method.

II.6. Biodiesel Characterization

The biodiesel characterization was performed in Soralchin oil refinery fuel analyzes laboratory, situated in Sbaa at Adrar city at southern Algeria. The analyzes are focused on the determination of the following parameters: Density was measured according to the method (ASTM D4052) using a DNA4500 density meter. Viscosity, Flash point for biodiesel produced from castor oil was measured according to ASTM D93 method. Pour point was measured according to ASTM D97 method. The cetane number of produced biodiesel is measured according to the distillation protocol of ASTM D86. Sulfur content was measured using X ray diffraction according to ASTM D4294 method. Calorific value was measured according to ASTM D1826.

III. Results and Discussion

Conventional oil seeds generally have water contents varying between 3 and 9% depending on the species and the variety. The average water content of castor seeds is 5.74%. This relatively low value makes it possible to lower the activity of the water which is responsible for the weathering reactions and to ensure good storage of the seeds. Many studies have shown that lowering the moisture content results in better oil yield [22].

The high rate of fat found in the castor oil plant seeds gives it an important potential in the oils' industries field. This percentage exceeds that of some conventional oilseeds such as pistachio 42.26% [23]. Castor seeds are very rich in oil 55% by weight of the shelled seed. The results obtained for the fat content are in agreement with other studies, who have reached an oil yield of 53% [23].

The analysis of the biochemical composition of the castor seed revealed a relatively high content of proteins in the order of 17%, while the ash content is 2.88%

Table 1 shows the characteristics of castor oil. The density found for our oil is 0.938, this value is very close to the value found by Alloune et al which is 0.9453 [23]. Comparing castor oil with other oils, we find that its density is higher than those of oils showed in table2.

Table 1. *Castor oil characteristics*

Characteristic	Value
Density at 20°C	0.9587
Acide value	1.148mg/g
Saponification value	185.83mg/g
Iodine value	87g/100g
Refractive index	1.477
Viscosity at 40°C	230.5 [mm^2/s]

Table 2. *Density of some vegetable oils*

Oil	Density g/cm^3 at 20°C	Refractive Index
Castor	0.938	1.477
Sunflower	0.920	1.472
Corn	0.919	1.470
Argan	0.917	1.4711
Coloquinte	0.909	1.474
Olive	0.910	1.466-1.468

The refractive index "R" of the oils varies according to their unsaturations, it increases with the degree of instauration of fatty acids contained in fat. In our case, the measured refractive index of castor oil is R = 1.477. This value agrees with other authors who give a value of the refractive index of castor oil around R = 1.473 [23]. By way of comparison, we give the refractive indices of some vegetable oils (see table 3), It is noted that castor oil has a refractive index close to that of the Coloquinte oil.

Table 3. *Refractive index of some oils*

Oils	Refractive index
Castor oil	1.477
Olive oil	1.466- 1.468
Sunflower oil	1.472
Argan oil	1.4711
Coloquinte oil	1.474
Sesame oil	1.470

The acid number indicates the degree of deterioration of the esters (essentially triglycerides) present in the fatty substance. The acid value of castor oil is 0.8976. Our result is close to that obtained by Alloune et al which gives a value of acid number of 0.901 [23].

The saponification index is related to the length of the fatty acids constituting the oil. The value of the saponification number found in this study is 182.325 (mg of KOH / g of oil). The saponification index of castor oil is close to that of olive oil, which varies between 184 and 196 mg of KOH / g of oil [23].

Viscosity is an important characteristic of fuels, it depends strongly on the temperature and directly influences the operation of the injection system, especially at low temperatures. The viscosity of castor oil is 230.5 mm^2 / s. Note that the viscosity of our castor oil is high compared to the value obtained by R. Alloune et al which gives a value of the viscosity of castor oil 185mm^2 / s at 40 ° C [23].

Biodiesel characterization

- **Yield of biodiesel**

The yield of biodiesel obtained by the transesterification reaction of castor oil is 91%, which is higher than that obtained by Alloun et al, which found a yield of 70% [23].

- **Biodiesel distillation**

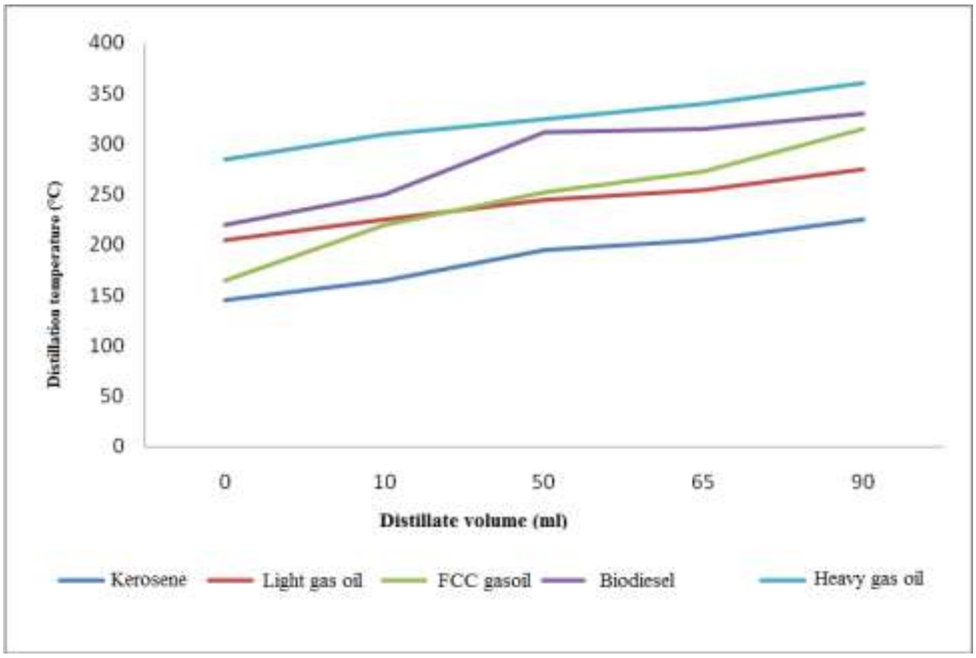

***Figure 3**. Distillation of biodiesel and various fuels*

Figure 3 shows that the distillation limit of biodiesel is at 330° C, at this temperature the distillation rate is 90% and beyond 330°C the biodiesel is degraded. This curve also shows that this biodiesel is composed of a mixture of products because the distillation curve has several stages, beyond 312°C the curve changes slope and at a distillation rate of 50% the curve becomes almost stable.

Below 220 ° C; there was no distilled fraction. This result shows that biodiesel does not contain water. Comparing biodiesel with other fuels we can say that our product is between heavy diesel and light diesel.

- **Density**

The density of biodiesel obtained from castor oil is 0.908 g/cm^3 This value remains higher than kerosene densities 0.780 g/cm^3; light gas oil 0.830 g/cm^3 and heavy gas oil 0.860 g/cm^3; but it is very close to that of the FCC gas oil which has a density of 0.900 g/cm^3 (The commercial diesel density is between 0.810 g/cm^3 and 0.860 g/cm^3 (SORALCHIN, 2018) Figure 4.

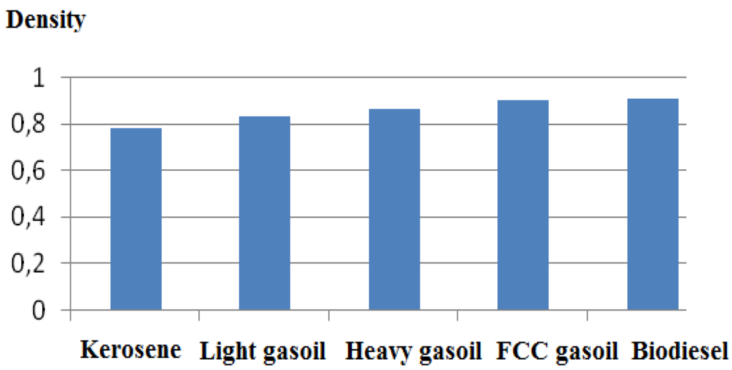

***Figure 4.** Histogram of densities of several fuels*

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- **Cetane number**

Cetane number Characterizes the self-ignition ability of diesel fuels, this characteristic is very important because it affects directly the proper functioning of combustion and the ignition delay (assessed the ability of a fuel to ignite). The obtained cetane number for the studied biodiesel is 36.05, this results is lower than the cetane number of the commercial diesel (48), but it is higher than that of the FCC gas oil (SORALCIHN, 2018).

It is possible to improve the castor biodiesel cetane number by mixing it with other fuels.

- **Sulfur content**

Sulfur dioxide comes mainly from the combustion of fossil fuels. At certain concentrations, it can cause eye, skin and respiratory irritation.

Our biodiesel contains 165ppm of sulfur; this value is five times lower than that of commercial diesel which contains 700ppm (SORALCHIN, 2018).

- **Pour point**

The pour point is the temperature at which the paraffin of the fuel crystallizes to the extent that the fuel freezes and no longer flows.

The pour point of the biodiesel treated in the present paper is -33°C; this value is lower than that of the national commercial diesel pour point, which varies according to the climate from -15 ° C in winter to -7 ° C in summer. (SORALCHIN, 2018).

- **Flash point**

The flash point is the temperature at which volatile substances are produced at a rate that allows them to be ignited in contact with a heat source: flame, spark. If the source of heat is removed, the ignition stops but not to maintain the combustion, its value is 130°C. This value lies in the European Standards for biodiesel.

The calorific value of Biodiesel issued from castor oil is 37.30 MJ/kg which lies in the European Standards for biodiesel which sets the maximum value to 120MJ/kg.

Table 4. *Physico-chemical analyzes of biodiesel and various fuels*

	Biodiesel from castor oil	kerosene	Light gas-oil	Heavy gas- oil	Gas-oil FCC
Cetane number	39.05	40-50	47-50	50-60	20-30
Viscosity [mm^2/s] at 40°C	12.90	0.01005	-	-	-
Density g/cm^3 at 20°C	0.91	0.78	0.83-0.84	0.860	0.90
Flash point [°C]	130	32-45	-	-	60-70
Pour point [°C]	-33	-	-	-	-
Sulfur content [ppm]	165	-	-	-	-
Calorific value (MJ/kg)	37.30	43.1-46.2-	-	-	-

IV. Conclusion

Castor plant is an energy and inedible plant. It grows very well in arid and semi-arid areas. The biochemical analysis of the seed of this plant gave the following results: a moisture content of 5.74%, 2.88% ash, 17% protein and 55% fat. The relatively low moisture content allows to lower the activity of the water and to ensure a good storage of the seeds.

The oil extracted from castor oil plant has very satisfactory physicochemical characteristics, and their characteristics corresponds to the standards' characteristics of the fossil fuel, except for the viscosity which remains important, and it can used as fuel. The Biodiesel obtained by the transesterification reaction of castor oil have a yield of 91% under the operating conditions (temperature reaction 60°C, 1wt% KOH and 9/1 methanol oil ratio).

The physical and chemical properties of biodiesel obtained from castor oil are interesting except for the cetane number which is lower than the commercial diesel standard, also the viscosity that is above the norm. Both characteristics can be improved by blending biodiesel with other fuels.

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Abbreviation and units

ASTM: American Society Testing Materials
SORALCHIN: Society Raffling Algerian-Chinese Gasoil
FCC: Gasoil Factory Cracking Catalytic
Ppm : Partie Par Million
RCO: *Ricinus Communis Oil*
AV: Acid Value

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