



Production and Characterization of Biodiesel from seed oil of Castor (*Ricinus communis* L.) plants

Awab W. AL-Harbawy and Mozahim K. AL-Mallah

Department of Biology, College of Education for Pure Sciences , University of Mosul , Mosul, Iraq

ABSTRACT

The investigation describe the hot and cold extraction methods used to produce oil from seeds of wild castor (*Ricinus communis* L.) plants. Cold extracted crude oil obtained by hydraulic press machine and refined by physicochemical techniques. Refined oil measurements were carried out according to the same parameters of crude oil. Physicochemical characters values of oil were : pH 6.7, moisture content 4.2%, glycerol wt. 5.3%, oil yield 47.6%, specific gravity 0.959, refractive index 1.477, acid value 3.12 mg KOH/g, iodine value 74.08 g I₂/100g, saponification value 181.52 mg KOH/g, kinematic viscosity 238 mm²/s and free fatty acids 1.56%. The data of hot extracted oil showed that these values were around the standard properties values of castor oil, while cold method oil was around some values and out of ranges in others. Interestingly, methanolysis was suitable to produce biodiesel from oils extracted either by cold or hot method. Evaluation of biodiesel exhibit superior properties of that produced by hot method. Some properties of cold extracted oil were similar to the standards and not in others.

Keywords: *biodiesel; extraction; crude oil; methanolysis; moisture; saponification; kinematic viscosity.*

1. INTRODUCTION

Castor (*Ricinus communis* L.) plant, of the Euphorbiaceae family commonly known as castor oil plant and Palma Christi. This plant was first found in Africa and then in both wild and cultivated states in tropical and subtropical countries (Caye *et al.*, 2008). Wild castor plant is well-adapted to arid conditions and able to stand drought for long periods (Carmen, 2010). Oil yield approximately 1413 liter per hectare in cultivated regions , seeds contain 35 – 55 % oil by weight for high yield breed type and it posses the highest viscosities among the vegetable oils of molecular weight 298 (Kulkarni and Sawant, 2003). Castor oil is one of few naturally occurring glycerides of high purity and 90% of the fatty acid is Ricinoleic acid (Akpan *et al.*, 2006). This coupled with its excellent solubility in methanol, it became the prior oil for transesterification to biodiesel, requiring a minimum amount of catalyst and heating that reducing production costs (Bello and Makanju, 2011).

Biodiesel fuel be defined as medium length (C16±C18) chains of fatty acids, comprised mainly of mono-alkyl fatty acid esters, non-toxic, biodegradable, sulphur and carcinogenic ring free components (Yamane *et al.*, 2001). Biodiesel, in comparison with diesel fuel had high cetane number permit its direct use as substitute fuel for diesel engines without any modifications or as a blending agent for diesel fuel (Penugonda and Venkata, 2012). Oil obtained from castor (*Ricinus communis* L.) seeds was chosen in this investigation due to the availability of this species as wild plants in our region and has no commercial uses.

2. MATERIAL AND METHODS

Preparation of seeds

Seeds were harvested from mature castor (*Ricinus communis* L.) plants of variety Zanzibariensis cultivated in field, dried, crushed and seeds were separated. The cleaned seeds were firstly sun dried for seven hours and then oven dried at 90°C to a constant weight to reduce the moisture content (Shridhar *et al.*, 2010). They were crushed to a size of 1.18 mm using mortar and pestle to rupture cell walls for easy oil extraction (Akpan *et al.*, 2006).

Oil Extraction and recovery

Cold method extraction of castor oil was established according to the standard method (Weiss, 1971) utilizing seeds press hydraulic machine of private company. Hot method extraction of castor oil was carried out in the laboratory (Edison *et al.*, 2012), aliquots of 50 ml isopropanol was weighed and placed in round bottom glass flask, to this 25 gm of the sample was put in thimble and settled in the center of the extractor and Soxhlet apparatus was heated at 108°C. The solvent boiled and vaporized through the vertical tube into the condenser at the top. The condensate liquid start dropping into the cotton wool thimble containing the sample and the extracted oil seeped through thimble into the flask via the siphon. After each hour the sample was dried at 70°C and weighed until the residue weight became constant. At this stage the amount of extracted oil was determined at the end of each extraction cycle, the oil-solvent mixture was oven heated at 108°C for solvent recovery. The percent yield of castor oil was calculated (Doan, 2004) using the following formula:

$$\% \text{ Yield} = \frac{Y1 - Y2}{Y1} (100)$$

Characterization of Castor Oil

Determination of Moisture Content of the Seeds

40gm sample of seeds was weighed, oven dried at 80°C for 7hrs. and the weight was recorded every 2hrs. until a constant weight was obtained. After each 2 hrs. , samples were removed from the oven, placed in desiccator for 30 min. to cool, then removed and re-weighed. The percentage moisture in these seeds was calculated (Akpan *et al.*, 2006) as in below :

$$\text{Moisture} = 100 (W_1 - W_2) / W_2 \%$$

W_1 = Original weight of the sample before drying

W_2 = Weight of the sample after drying

Determination of Oil Yield

30gm seeds sample was placed in the thimble and approximately 150ml of isopropanol was poured in the round bottom flask and heated at 180°C for 3hrs. continuous extraction using Soxhlet apparatus. The experiment was repeated with weights of 35g, 40g and 50g. Finally, solvent was distilled and the percent of oil extracted was determined (Akpan *et al.*, 2006).

Determination of pH Value

Samples of 2gm was each poured into 25ml glass beaker, 13ml of hot distilled water was added to each sample and stirred slowly. The mixtures were then cooled in a cold-water bath to 25°C. The pH meter electrode was standardized with buffer solution and then immersed into the sample and pH value was measured (Akpan *et al.*, 2006).

Determination of Specific Gravity

Density bottle of 5ml capacity was weighed (W_0), filled with oil, then stopper inserted and reweighed (W_1). The oil was substituted with water after washing and drying the bottle and weighed (W_2). The expression for specific gravity is:

$$\text{Sp.gr} = (W_1 - W_0) / (W_2 - W_0) = \text{Mass of the substance} / \text{Mass of an equal volume of water (Akpan et al., 2006)}$$

Determination of Refractive Index

Few drops of oil samples were transferred to glass slide of the refractometer (ATAGO Co. Ltd. Japan). Through the eyepiece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross, In this case the pointer on the scale pointed to the refractive index and values were recorded (Akpan *et al.*, 2006).

Determination of Kinematic Viscosity

Viscometer of flow time above 200 seconds was elected (Cannon Fenske Opaque, Bransted international , Glass

capillary viscometer), charged with the sample by inverting the tube's thinner arm into the liquid sample . Suction force drawn up to the upper timing mark of the viscometer (Fig.1), then the instrument was turned to it's normal vertical position.



Figure.1 Glass capillary viscometer (Cannon Fenske)

The viscometer was held by metal holder and inserted in a water bath at 40°C for approximately 10 min. to allow the sample to reach bath temperature. The suction force was then applied to the thinner arm to draw the sample slightly above the upper timing mark. The afflux time by timing the sample free flow from the upper timing mark to the lower timing mark was recorded (Akpan *et al.*, 2006).

Determination of Acid Value

25ml of each of diethyl ether and ethanol was mixed in a 250ml beaker, then was added to 10gm of oil contained in a 250ml conical flask and few drops of phenolphthalein were added . The mixture was titrated with 0.1M NaOH to the end point with consistent shaking, a dark pink color was observed and the volume of 0.1M NaOH (V_0) was recorded.

Free Fatty Acid (FFA) was calculated (Akpan *et al.*, 2006; Kyari, 2008) as in below.

$$V_0 / W_0 \cdot 2.82 \cdot 100$$

$$100\text{ml of } 0.1\text{M NaOH} = 2.83\text{gm of oleic acid}$$

$$W_0 = \text{sample weight}$$

$$\text{Then, acid Value} = \text{FFA} \cdot 2$$

Determination of Saponification Value

Two grams of oil sample was weighed into a conical flask and 25ml of 0.1N ethanolic potassium hydroxide (KOH) was added. The mixture was constantly stirred and allowed to boil gently for 60min. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator

were added to the warm solution and titrated with 0.5M HCl to the end point until pink color of the indicator disappeared. The same procedure was used for other samples and blank. Saponification value was calculated (Akpan *et al.*, 2006; Kyari, 2008) as in below:

$$S.V = 56.1 N(V_0 - V_1)/M$$

V_0 = volume of the solution used for blank test

V_1 = volume of the solution used for determination

N = Actual normality of the HCl used

M = Mass of the sample

Indicator method was used as specified by ISO 3657 (1988).

Determination of Iodine Value

Samples of 0.4gm of oil was weighed into a conical flask and 20ml of carbon tetra chloride (CCl₄) was added to dissolve the oil. Then 25ml of Dam's reagent was added to the mixture using a safety pipette in fume chamber. Stopper was inserted and the content of the flask was vigorously swirled. The flask was placed in the dark for 2 and half hrs. Then, 20ml of 10% aqueous potassium iodide (KI) and 125ml of water were added using a measuring cylinder. The solution was titrated with 0.1M sodium thiosulphate (Na₂S₂O₃) solutions until the yellow color almost disappeared. Few drops of 1% starch solution indicator was added and titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (I.V) is given by the expression:

$$I.V = 12.69 C(V_1 - V_2)/M$$

C = Concentration of sodium thiosulphate used

V_1 = Volume of sodium thiosulphate used for blank

V_2 = Volume of sodium thiosulphate used for determination

M = Mass of the sample (Akpan *et al.*, 2006; Kyari, 2008)

The method specified by ISO 3961 (1989) was used.

- **Refining of Extracted Oil**

Degumming and Neutralization

Extracted oil was degummed by the addition of boiling water, stirred for 2 min. and allowed to stand in the separating funnel and the aqueous layer was removed. The procedure was repeated to ensure removal of most gums. For neutralization, about 60gm sample of degummed oil was placed into a beaker and heated to 80°C, then 40ml of 0.1M NaOH was added and stirred to a uniform solution. Sodium chloride (about 10% of oil weight) was added to help settle out the soap formed, then transferred into a separating funnel, allowed to stand for 1h and the soap was separated from the oil. Hot water was added again and again to the oil solution until the soap residues was

3. RESULTS AND DISCUSSION

The data in table (1) expressed the physicochemical properties of oil extracted from castor seeds by cold and hot method.

Table.1 Physicochemical properties of oil extracted from castor (*Ricinus communis* L.) seeds by cold and hot methods

		Cold Method Castor Oil
Parameter	Unit	

removed and the neutralized oil was drawn off into beaker (Nkpa *et al.*, 1989; Carr, 1976).

- **Bleaching**

Sample (50gm) of neutralized oil was placed in a beaker, heated to 90°C, activated clay (15% of oil weight) was added and the mixture was stirred continuously for 30 min. The temperature was allowed to rise up to 110°C for another 30 min. and mixture was filtered in an over at 70°C (Nkpa *et al.*, 1989; Carr, 1976).

- **Modification of the Refined Castor Oil: Sulphation**

Twenty grams of oil was warmed at 35°C, to this 15ml of 98% sulphuric acid (H₂SO₄) was added and the reaction was allowed to completion with constant stirring. The product was washed up with hot distilled water and left to stand for 2 hrs., after which water was removed. The sulphuric acid ester formed was finally neutralized with 10ml of 0.1M sodium hydroxide (NaOH) (Nkpa *et al.*, 1989; Carr, 1976).

Producing Biodiesel from Castor Oil

The following basic steps was followed (Penugonda and Venkata, 2012) to Produce Biodiesel from castor oil

- One liter of castor oil is taken.
- Add 300-330 ml of methanol & 10 ml of concentrated sulphuric acid to oil.
- The temperature of this mixture is to be set at 65-70 °C and to be maintained for about 6 hrs. with continuous stirring.
- The mixture was allowed to settle for 8 hrs. at the above degree after completion of this reaction.
- The settled reactant mixture would consist of two layers, the upper layer as biodiesel and traces of glycerin etc. and the bottom layer as glycerin and gums etc.
- Glycerin was removed from the biodiesel preparation unit by opening the tap provided on the bottom and this pre washed biodiesel is transfer to a separating funnel.
- Add 200 ml of hot water at approximately 40° C per liter of crude biodiesel with shaking and allowed to settle to separate two layers for nearly 7-8 hrs.
- Repeat the above step at least three times to eliminate traces of glycerin and soap from the biodiesel yield.
- Adjusting viscosity esterified castor oil by further treatment with mineral turpentine oil (M.T.O.).

		Crude	Refined	Hot method Castor Oil
pH	----	6.3	6.5	6.7
Moisture content	%	3.3	3.3	4.2
Extraction Yield	%	32.4	32.4	47.6
Specific gravity	----	0.960	0.952	0.959
Glycerol wt.	%	7.45	8.35	5.30
Kinematic Viscosity at 40 °C	mm ² /s	243	241	238
Acid value	mg KOH/g	5.68	5.92	3.12
Iodine value	g I ₂ /100g	71.12	62.23	74.08
Free fatty acid	%	2.84	2.96	1.56
Refractive index	----	1.476	1.475	1.477
Saponification value	mg KOH/g	185.04	173.16	181.52

The obtained results of moisture content were varied from those recorded by the other researchers variation from the literatures (Salunke and Desai, 1941) which was between 5 to 7 %. The oil yield fall within the standard range of oil content 30–55% of castor seeds (Marter, 1981; Weise, 1983) depending on the variety.

The data in the above table indicate that both methods can be utilize to produce oil from castor seeds. Concerning the quality of oil produced, hot method is favorable. It seems likely that physicochemical properties of oil produced in this study was identical to those reported in other studies using the same plant species (Encinar *et al.*, 2010; Hemant *et al.*, 2011).

Viscosity value of crude castor oil was 243 mm²/s and of refined oil was 241 mm²/s, this may be attributed to the fact that some impurities and other components were removed during refining (Akpan *et al.*, 2006). There was slight

difference between refractive index of hot method oil and cold method oil (crude and refined). but comparing this result with ASTM values that ranges from 1.476 – 1.479 the hot method oil and crude oil fall within the range, while a minor difference is noticed with refined oil. However, this difference can be considered being within an acceptable experimental error range.

Values of pH were varied between cold and hot extracted oil, this may due to degumming and neutralization carried out during the refining process (Akpan *et al.*, 2006). Glycerol weight of cold extracted oil was higher than that of hot extracted oil, this may be explained to the extraction procedure using isopropanol as a solvent and to the high temperature used in the hot method extraction. Generally, the chemical properties indicates that acid value, Saponification value and Iodine value of all oils were around the standard values of castor oil (Akpan *et al.*, 2006).

The results in table (2) exhibit the physicochemical properties of biodiesel produced from castor oil.

Table.2 Physicochemical properties of biodiesel produced from oil extracted from castor (*Ricinus communis* L.) seeds by cold and hot method

Parameter	Unit	Cold method oil Biodiesel		Hot method Biodiesel
		Crude	Refined	
pH	----	6.5	6.7	6.1
Specific gravity	----	0.952	0.942	0.924
Kinematic Viscosity at 40 °C	mm ² /s	24.9	24.6	23.8
Acid value	mg KOH/g	4.36	5.48	3.80
Iodine value	g I ₂ /100g	62.23	71.12	58.34
Free fatty acid	%	2.18	2.74	1.90
Refractive index	----	1.470	1.468	1.467
Saponification value	mg KOH/g	181.10	171.04	179.06
Flash point	°C			
Water and sediment	% volume	< 0.050	< 0.050	< 0.050

The results mentioned in the above table refer to the differences among the physicochemical properties of the three types of biodiesel produced from crude, refined and hot methods (Fig. 2). The pH values, Specific gravity, Kinematic Viscosity, Iodine value and free fatty acid of hot method biodiesel was

less than the values of cold method biodiesel. This perhaps due to the different procedures of oil extraction and refining steps using various chemicals as solvents or neutralizers. Interestingly the water and sediment results was within the ASTM acceptable range.

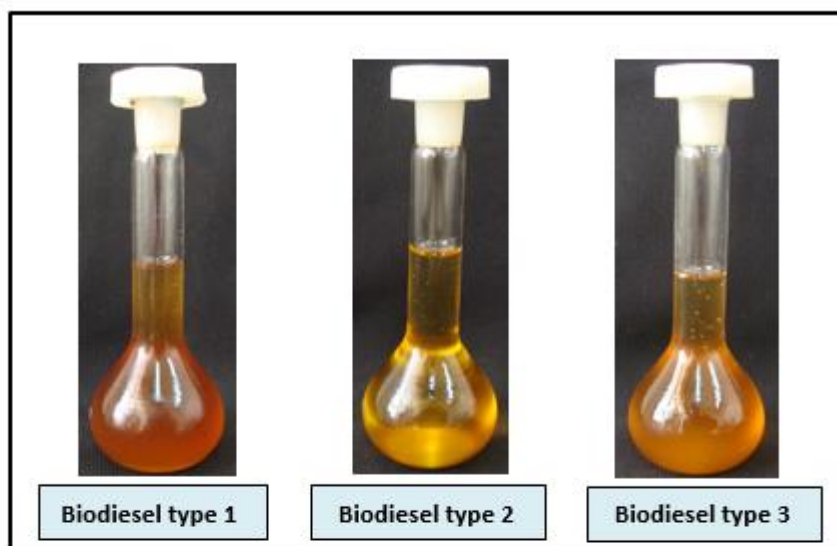


Figure.2 Three types of biodiesel produced from oil of Castor (*Ricinus communis L.*) seeds

- (1) Biodiesel produced by hot method oil.
- (2) Biodiesel produced by refined oil.
- (3) Biodiesel produced by crude oil.

The conclusion is that the hot extraction method was better than the cold method due to the high oil yield, good quality and could be recommended for industrial usage. Interestingly, biodiesel fuel quality was mostly suitable to comply with most of standard aspects.

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