



## Synthesis and characterization of biodiesel from seeds of castor plant

Muna Mahmood Khudhair, <sup>a,\*</sup> Enaam Fadil Mousa, <sup>b</sup>

<sup>a,b</sup> Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq.



### Abstract

As fuel resources decline and global warming, the quest for a renewable, sustainable and more environmentally friendly fuel source continues. This article was aimed to extract the oil from castor plant seeds and use it in the production of its ester. Solvent extraction method was employed to produce castor oil from Iraqi castor plant seeds using hexane as solvent and yielded 23.800%. The chemical properties of hexane extract studied were: acid value, free fatty acid, saponification value, and iodine value of 0.885 mg KOH/g, 0.445 mg KOH/g, 175 mg KOH/g, 85 g I<sub>2</sub>/100g oil respectively. The physical properties of hexane extract reported were: density at 15 °C, viscosity at 40°C, refractive index of 961.200 kg M<sup>-3</sup>, 213.580 mm<sup>2</sup>/s, 1.4674 respectively. Also, transesterification reaction of castor oil was applied to produce castor biodiesel using methanol and KOH as catalyst. The chemical properties of methyl ester of castor oil studied were: acid value, free fatty acid, saponification value, and iodine value of 1.038 mg KOH/g, 0.522 mg KOH/g, 183 mg KOH/g, 87 g I<sub>2</sub>/100g oil respectively. The physical properties of its ester found were: density at 15 °C, viscosity at 40°C, refractive index of 906.160 kg M<sup>-3</sup>, 17.244 mm<sup>2</sup>/s, 1.466 respectively. The castor oil and its methyl ester were characterized by utilizing FTIR and NMR spectroscopic techniques.

**Keywords:** Biodiesel, Castor oil, Alkyl ester of fatty acids, Oil extraction, Castor seeds.

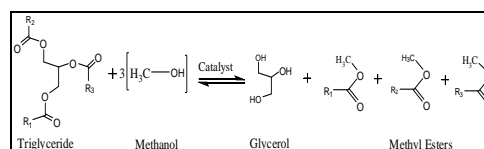
### 1. Introduction

The demand for alternative fuel is a crucial topic since the production of fuel from petroleum is declining. Biodiesel has received more attention in recent years as a renewable with less pollutant emissions compared to classical fuel on its combustion [1-2]. In the ASTM (American Society for Testing and Materials), biodiesel is a type of fuel that is monoalkyl esters of fatty acids, produced from plant or animal lipids [3-4].

Large numerous of vegetable oils have been used in the production of biodiesel. The plant of castor bean (*Ricinus communis* L.) refers to the Euphorbiaceae family which grows naturally over wide areas of geographical regions. This plant is a tropical kind, and it may grow in hot regions. Studies have shown that the oil of castor bean plant accounts for about 30-35% of the plant's total oil content. There are various methods, including solvent extraction and presses, for extracting this. The fruit should be heated before pressing, and then solvent extraction should be used.

Castor oil and its compounds are utilized in the manufacture of chemical compounds that are inserted in paints, lubricants, detergents industries and others [4]. Nowadays, the most important use of castor oil is produced biodiesel by transesterification with alcohols that have short chain aliphatic. This process reduces viscosities of oils without decreasing its calorific power, thereby, stating their use as fuel and methanol is the main preference alcohol in transesterification reaction [5].

This process is a sequence of three stepwise reversible reactions in which the triglycerides are converted to diglycerides, monoglycerides respectively and produced a by-product (glycerol GL). One mole of fatty acid ester is resulted in each step [6] (equation). Overall reaction:



Scheme 1: Transesterification reaction [7]

\*Corresponding author e-mail: [muna.m@csw.uobaghdad.edu.iq](mailto:muna.m@csw.uobaghdad.edu.iq); (Muna Mahmood Khudhair).

Receive Date: 25 July 2022, Revise Date: 03 August 2022, Accept Date: 29 August 2022.

DOI: [10.21608/EJCHEM.2022.152391.6600](https://doi.org/10.21608/EJCHEM.2022.152391.6600)

©2023 National Information and Documentation Center (NIDOC).

### The chemical reaction that take place in stages

1. TG(triglyceride) + ROH  $\leftrightarrow$  DG (diglycerides) + RCO<sub>2</sub>R
2. DG + ROH  $\leftrightarrow$  MG (monoglycerides) + RCO<sub>2</sub>R
3. MG + ROH  $\leftrightarrow$  RCO<sub>2</sub>R + GL(glycerol)

Biodiesel is produce by base catalyzed trans esterification of castor oil which is common method because of cheapest method than others (8). But this unsuitable technique when oils with a high concentration of free fatty acids (greater than 3%)[9]because the latest reacts with base to form soap, then gel formation in addition it complicated the separation of product[10].

So, this research is based in refined the castor oil through degumming, neutralization, and bleaching with Iraqi bentonite after extraction castor plant seeds with hexane and evaluate physicochemical properties of it.

Also, the main objective of this study was to synthesis castor biodiesel from refine castor oil and determine physicochemical properties and compare them with those of ASTM specification of biodiesel available in literature. In addition, characterization the castor oil and its methyl ester using Fourier transform infrared (FTIR) and NMR were applied in this research.

## 2. Experimental

### 2.1. Materials

Methanol, hexane, and potassium hydroxide were of analytical reagent grade and were supplied from SIGMA COMPANY.

- Castor beans are obtained from Altaji town in Baghdad in Iraq in the April of 2020.
- Iraqi bentonite came from the StatebCompany for Geological Survey and Mining, and its chemical composition is illustrated in table1.

Table 1: Iraqi bentonite's chemical composition

Material	Percentage Weight (%)	Material	Percentage weight (%)
SiO <sub>2</sub>	54.07	MgO	3.20
Fe <sub>2</sub> O <sub>3</sub>	5.59	K <sub>2</sub> O	0.57
CaO	5.65	L.O.I.	12.40
SO <sub>3</sub>	1.10	O.M	7.19
Na <sub>2</sub> O	0.87	Moisture	0.47
Cl	0.92	C.E.C.	76.59
Al <sub>2</sub> O <sub>3</sub>	15.05	Total C.	0.93
TiO <sub>2</sub>	0.79	Mon	77.00

L.O.I; Lost on ignition, O.M ; Organic Matter, C.E.C.; Cation exchange capacity, Mon;Montmorillonite

## 2.2. Methods

### 2.2.1. Castor Oil Extraction

#### 2.2.1.1. Castor Beans Processing

The castor beans plant undergoes clearing, drying, winnowing, and grinding processing in the preparation for extraction process.

#### 2.2.1.2. Solvent extraction of castor oil

A round bottom flask was filled with 300ml of hexane. We put 10g of castor beans in thimble of the soxhlet extractor. The mixture heated to 60 °C. to about 120 min., The solvent vaporizes and rises up through the tube into the condenser. when the solvent was boiling. The liquid condensate slowly drips into the castor bean container. The extract enters the flask containing the solvent after passing through a thimble and down a siphon tube. After the completion of extraction process, the solvent was removed by distillation to produce the castor oil [11].

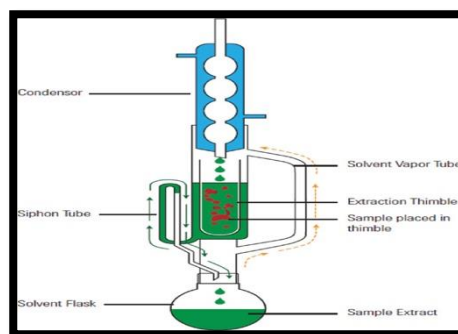


Figure 1 : Soxhlet apparatus used for castor oil extraction[12].

#### 2.2.1.3. Refining of castor oil

##### 2.2.1.3. 1. Degumming and Neutralization

The extracted oil was degummed with boiling water, stirred for two minutes, and then allowed to separate using a separating funnel. To guarantee that all gums were removed, the procedure was performed numerous times. 60g of oil and 40ml of 0.1M NaOH were heated at 80°C to create a homogeneous solution for the neutralization process. Following that, sodium chloride (approximately 10% of the weight added) was used to separate the soap that had been created in a separating funnel. To ensure the removal of soap, boiling water was then added [13, 14].

##### 2.2.1.3. 2. Bleaching

To activate the bentonite, (2M) of hydrochloric acid was added to the bentonite and the mixture was heated and boiled at about 100°C for two hours. It is then filtered, washed the mixture several times with water and finally dried and

ground [15]. Pour 50g of neutralized oil was into a beaker and heat to 90°C. Activated bentonite 15% weight of oil was added. The mixture was continuously stirred thirty minutes along. Let the temperature rise to 110°C for another thirty minutes. The por was filtered and weighed three times and takes the average[14].

### 2.2.2. Transesterification Process of castor oil

Potassium hydroxide (3 g/liter) was added to methanol (18 moles) in a round bottom flask with stirring at 350 rpm until it is dissolved. Then, castor oil (1mole) was added to the mixture in a reactor that equipped with a heater/magnetic stirred and heated the mixture for 6 hours at 60 C°. The mixture was let to settle into two layers of biodiesel and glycerol, with the bottom layer being denser. A separating funnel was used to separate the mixture. Hydrochloric acid solution (1%) was added to the biodiesel phase to react with catalyst (remaining base) after that washed by using distilled water to remove the mixture from impurities like(di, monoglyceride,catalyst, soap and excess methanol). The washing process was repeated three times, and then dried by using magnesium sulfate.

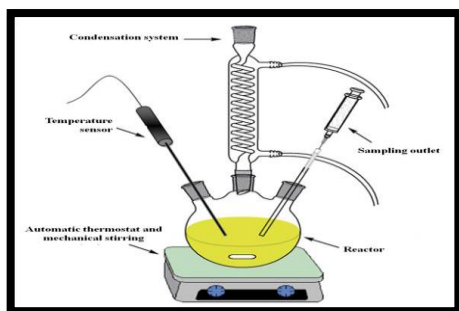


Figure 2: Experimental transesterification system[16].

### 2.2.3. Analysis of products

The analytical techniques were used to characterize the products. Kinematic viscosity was measured using Cannon-Fenske viscometer, size 100, ABBE Acid value is important indication of the quality of castor oil[17,18]. In literature survey, the range of acid value of castor oil is from 0.140-1.970 mg sodium hydroxide for (1)gram of oil [17,19-21]. Table 3 showed that the acid value of crude and refined castor oil is 1.591 mg and 0.885mg sodium hydroxide for (1)gram of oil respectively. Higher amount is noticed in crude oil because the presence of free fatty acid while it less in refined oil as a result of alkali neutralization process in refining treatment. In addition, both values are within the range limits of

ASTM specification. The same case was shown about the free fatty acids.

Saponification value is chemical property of oil that used to evaluate the molecular weight of triglyceride [22]. A number of studies revealed that the range of saponification value is from 165.500-187.000 mg potassium hydroxide for 1 gram of oil[22]. As shown in table 3 the values of saponification of the crude and refined castor oil were found to be 185mg potassium hydroxide for 1 gram of oil and 175mg potassium hydroxide for 1 gram of oil respectively. As appearance, the crude oil has more saponification value than the refined oil because the crude oil required more alkaline to neutralize the free fatty acid in the oil as compared with the refined castor oil. The highly comparable was observed upon crude and refined castor oil about saponification value with ASTM specification of castor oil.

Iodine value indicates the unsaturation level of oils. The higher iodine values reveals higher level of unsaturation and vice versa. The studies fixed that the range of iodine number is 83-93 g I<sub>2</sub>/100g oil (21-22). As obvious from table(3), the results obtained for the Iodine value of crude oil and refined oil were discovered 87.72 g I<sub>2</sub>/100g oil and 84.80 g I<sub>2</sub>/100g oil respectively and both have good agreement with ASTM specification of castor oil.

refractometer was used to record refractive index at 40 °C, acid value was accounted by titration with ethanolic potassium hydroxide in the presence of phenolphthalein as indicator.

Fourier transform infrared spectrometry (FTIR) was applied to characterize the functional groups that found in castor oil and its methyl ester using Shimadzu model 84005 FTIR.

The production of biodiesel was determined by Bruker Ascend 600 hz 1 H NMR Spectroscopy with deuterated chloroform, CDCl<sub>3</sub> used as solvent.

## 3. Results and Discussion

### 3.1. Study the properties of castor oil

The oil percentage of castor oil depends on the nature of castor seeds and the difference of solvent in extraction which it ranged from 20-55% [17]. So, in the present study it was found that the percentage of oil and moisture content were 23.8 and 4.30 % respectively as shown in table 3 which is illustrate the chemical and physical properties of refined and crude castor oil as well as the ASTM specification of castor oil.

Table 3: Physicochemical properties of refined and crude castor oil with ASTM specification

Property	Units	Present study		ASTM
		Refined castor oil	Unrefined castor oil	
Oil yield	%	23.800	-	-
Moisture content %	%	4.300	-	-
Acid value	mg KOH / g	0.885	1.591	0.4-4.0
Free fatty acid	mg KOH / g	0.445	0.800	-
Saponification Value	mg KOH / g	175	185	175-187
Iodine value	g I <sub>2</sub> /100g	85	87.720	82-88
Density at 15 °C	kg M <sup>-3</sup>	961.200	961.20	0.957-0.968
Viscosity at 40°C	mm <sup>2</sup> /s	213.580	248.340	258.01
Refractive index	-	1.4674	1.4686	1.476-1.479
Solubility in alcohol	-	Complete	Complete	Complete
Color	-	Amber	Dark brown	Amber

Acid value is important indication of the quality of castor oil [17,18]. In literature survey, the range of acid value of castor oil is from 0.140-1.970 mg NaOH/g of oil [17,19-21]. Table(3) showed that the acid value of crude and refined castor oil is 1.591 mg sodium hydroxide for (1)g of oil and 0.885mg sodium hydroxide for (1)g of oil respectively. Because free fatty acids are present in crude oil, the value is higher there, whereas it is lower in refined oil as a result of the alkali neutralization process during refining. In addition, both values are within the range limits of ASTM specification. The same case was shown about the free fatty acids.

Saponification value is chemical property of oil that used to evaluate the molecular weight of triglyceride [22]. A number of studies revealed that the range of saponification value is from 165.500-187.000 mg KOH/g of oil[22]. As shown in table 3 the values of saponification of the crude and refined castor oil were found to be 185mg KOH/g of oil and 175mg KOH/g of oil respectively. As appearance, the crude oil has more saponification value than the refined oil because the crude oil required more alkaline to neutralize the free fatty acid in the oil as compared with the refined castor oil. The highly comparable was observed upon crude and refined castor oil about saponification value with ASTM specification of castor oil.

Iodine value indicates the unsaturation level of oils. The higher iodine values reveals higher level of unsaturation and vice versa. The studies fixed that the range of iodine number is 83-93 g I<sub>2</sub> /100g oil [21-22]. As clear from table 3, the results obtained for the Iodine value of crude oil and refined oil were found 87.72 g I<sub>2</sub> /100g oil and 84.80 g I<sub>2</sub> /100g oil respectively and both have good agreement with ASTM specification of castor oil. The values of density for crude and refined castor oil are observed to be the same 961.200. This result is in agreement with the ASTM standard reported in literature [23]. Differences were obtained between the value of viscosity for the crude and refined castor oil. The values of the viscosity of the crude and refined castor oil were found 248.34 and 213.580 respectively. These results were found to be outside the ASTM specification of biodiesel recommended standard range (6.3 – 8.8st) [4], while the refined oil's viscosity of is quite within range. This may be referred to the presence of some impurities and other components which were removed during refining. The higher value of kinematic viscosity of castor oil attributed to hydroxyl group that found in ricoleic acid which is the predominant among fatty acids in castor oil[24]. As apparent from table 3, there is no significant difference between the refractive index values obtained for crude oil, 1.4680 and that of the refined oil, 1.4677. A little difference is noticed when comparing these results with the values of ASTM specification that ranges from 1.476 – 1.479. However, due to the existence of some contaminants and other components in the crude oil combination, this may be regarded as an acceptable error range. Thus, the values of refractive index for crude and refined castor oil were in good agreement with ASTM specification of castor oil.

As clear from the above results, there is some differences between the properties of crude and refined castor oil may be refer to refining process of crude castor oil which include degumming that is used to reduce or remove the metal content and phosphatides that present. In the present study, water degumming was applied because it was simple and inexpensive method [25]. Neutralization is the second step of refining of crude castor oil which is used to reduce free fatty acid content that was increased with the long time stored more than 12 months of castor oil and the presence of moisture[26]. Alkali neutralization was used to reduce FFA, oxidation products, residual metals, proteins, and carbohydrates [27]. The third step of refining process is bleaching which is very important treatment to gain castor

oil without colored bodies, antioxidants, and remaining phospholipids [28]. Activated Iraqi bentonite was applied in present study to bleach the castor oil through adsorption process to improve the appearance of castor oil.

### 3.2. Study the properties of biodiesel castor oil

Table 4 acts the properties of biodiesel castor oil with ASTM specification. This biodiesel castor oil was produced with the conditions: Potassium hydroxide (1 wt.%) acts the catalyst, and molar ratio 18:1 (methanol/oil), 45 °C and 700 rpm.

Density is an important fuel property, which affects the mass of injected fuel into the air-fuel chamber and thus affects the engine performance. The pumps of fuel injection meter it by volume and the more density fuel has larger mass in same volume. So, the density of fuel has effect on engine output power [29]. It has been discovered that the density of biodiesel depends on the esters and residual alcohol levels; as a result, vegetable oil affects density [30]. In this study, the densities for castor oil that used and the obtained biodiesel were 961.20 kg/m<sup>3</sup> and 906.16 kg/m<sup>3</sup> respectively. Though the lowering about (5.726%) is the close to that of biodiesel produce from other oils [30, 31], the resulted value of density is not within the limits of ASTM values. So, the improvement of this property with mixtures must be done.

The higher kinematic viscosity of fuel causes higher formation of engine deposits due to the increasing of internal friction of layers of fuel moving over others [16]. As illustrated from table 4, castor biodiesel has kinematic viscosity value 17.244 mm<sup>2</sup>/s, while the castor oil has (213.580 mm<sup>2</sup>/s), so, the reduction of kinematic viscosity is about 91.926% through transesterification and this result is very close to that obtained from Encinar et al., [16] which revealed that the reduction is about 94.2%. The kinematic viscosity of castor biodiesel is outside of the range of ASTM specification, so it should be mixed with mineral fuel or other esters to correct the value.

Table 4 shows that refractive index value of methyl ester of castor oil was 1.4676. Little differences between studies may be refer to differences in study condition, the nature of castor oil, and planting and harvesting conditions. In general, presence of impurities in the oil has effect on refractive index value (32).

Table 4: physical - chemical properties of biodiesel castor oil with ASTM biodiesel standard specification

Property	Units	Current study	EN 14214	ASTM D6751	Method
Ester content %		98			ASTM
density (15 °C)	kg M <sup>-3</sup>	906.16	860-900	875-900	ASTM D4052
Kinetic viscosity at 40°C	mm <sup>2</sup> /s	17.244	3.5-5.0	1.9-6.0	ASTM D445
Refractive index		1.4676			ASTM D1218
Acid value	mg KOH/g	1.038	<0.5	<0.8	ASTM D664
Free fatty acid	mg KOH/g	0.522	-	-	
Saponification value	mg KOH/g	183	-	-	ASTM D5558
Iodine value	g <sub>2</sub> /100g	87	120 max	115 max	ASTM D 1959-97

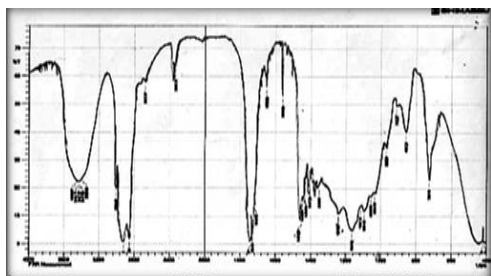
The acid value of castor biodiesel was 1.038 mg NaOH/g, as shown in Fig. 4, which indicates an increase (Table 4). ASTM specifications state that the acid number must be between 0.5 and 0.8 mg KOH/g. However, it has been demonstrated that the biodiesel's acid value is outside of the accepted range because of its high fatty acid (ricinoleic acid) concentration [33]. The saponification value rises as the molecular weight drops [34]. Castor biodiesel had a saponification value of 183, as shown in table 4, and this result is comparable to that reported by Encinar et al. [16]. There is no saponification value disclosed by the ASTM or the European Biodiesel Standard EN 14214 [35, 36]. The amount of iodine in a vegetable oil depends on its composition; both the oil and its ester should have the same amount [34]. In Table 4, the iodine number is within the limits of ASTM specification.

### 3.3. Instrumental analysis of castor oil and its methyl ester

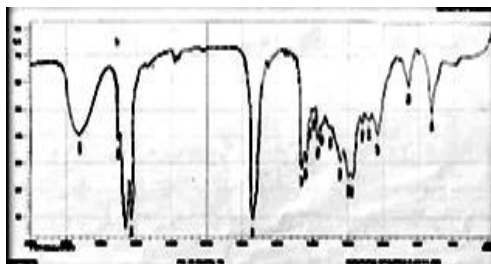
#### 3.3.1. Fourier Transform Infrared Spectrophotometric

The FTIR spectra were used to identify the functional groups that found in expected product through the appearance of absorption bands at different vibrations.

The absorbance band at about  $3420\text{ cm}^{-1}$  refers to the stretching vibrations O-H group which approved the presence of hydroxyl group in fatty acid (ricinolic acid that is the prominent in castor oil). The band at  $3007\text{ cm}^{-1}$  notices the C-H vibrations of cis-isomer of double bond of unsaturation fatty acids, whereas the absorption bands at  $2922$  and  $2855\text{ cm}^{-1}$  are represents vibrations (asymmetrical and symmetrical) of  $\text{-CH}_2$  aliphatic fatty acid [37,38]. The carbonyl(C=O) group for ester appears characteristic Absorption band for Triglyceride at ( $1739\text{ cm}^{-1}$ ). Scissoring bending vibrations for ( $\text{-CH}_2$ ) aliphatic groups showed at  $1455\text{ cm}^{-1}$ , while the absorption bands at  $1366$  and  $1235\text{ cm}^{-1}$  are refer to bending vibration for  $\text{-CH}_2$  aliphatic groups. The absorption bands at  $1235$ ,  $1160$ ,  $1089$  and  $1040\text{ cm}^{-1}$  belong to C=O group (bending vibrations). The ( $971\text{ cm}^{-1}$ ) band bending out of plane approved that the presence of double bond  $\text{-HC=CH-}$ (*trans*). The  $\text{=CH}_2$  wagging vibrations band appeared at  $858\text{ cm}^{-1}$ . However the  $719\text{ cm}^{-1}$  band is refer to overlapping of cis-disubstituted olefins, approves that the fatty acids are long chain



A



B

Figure 3: FTIR spectra of A(castor oil), B(its methyl esters)

The Fourier Transform Infra Red analysis of biodiesel shows that the presence of  $\text{-OH}$  through  $3400\text{ cm}^{-1}$  band, C-H aliphatic through  $2900\text{ cm}^{-1}$  band, C=O ester group through  $1720$

$\text{cm}^{-1}$ , C-H through  $1400\text{-}1500\text{ cm}^{-1}$  band, C-O at  $1140\text{ cm}^{-1}$ , the presence of C-H out of plane at  $700\text{-}850\text{ cm}^{-1}$  [39-41].

Comparison of FTIR spectra of biodiesel castor oil and its parent oil appeared of some absorption bands such as strong peak at  $1720\text{ cm}^{-1}$  related to ester group and peaks at  $1168\text{ cm}^{-1}$ ,  $1195\text{ cm}^{-1}$ , disappeared of absorbance at  $1500\text{-}1700\text{ cm}^{-1}$ , at  $1800\text{-}2500\text{ cm}^{-1}$ , and  $968\text{ cm}^{-1}$ , split the band of  $1454\text{ cm}^{-1}$  to  $1463\text{ cm}^{-1}$  and  $1436\text{ cm}^{-1}$  related to functional group  $\text{CH}_3$ , appearance of  $1168\text{ cm}^{-1}$ ,  $1195\text{ cm}^{-1}$  bands, and disappearance of absorption band  $968\text{ cm}^{-1}$  which means that the cleavage of triglycerides was achieved [42].

### 3.3.2. NMR spectroscopy

$^1\text{H}$  NMR spectroscopy was applied to a sample of castor oil and its methyl ester. Figs 4A and 4B represent their  $^1\text{H}$ - NMR spectra respectively. In the  $^1\text{H}$ NMR of castor oil, different peaks were observed d 5-5.5 ppm ( $\text{CH=CH-}$ ), d 4-4.1 ppm ( $\text{-CHOCOR}$ ), d 2.3 ppm ( $\text{-CH}_2\text{COOR-}$ ), d 2.1 ppm ( $\text{CH=CHCH}_2\text{CHOH}$ ,  $\text{CH=CHCH}_2\text{CHOCOOR}$ ), d 1.9 ppm ( $\text{CH}_2\text{CH}_2\text{CH=CH}$ ), d 1.5 ppm ( $\text{CH}_2\text{CH}_2\text{COOR}$ ), d 1.1-1.3 ppm ( $\text{CH}_2$ ), and d 0.6-0.9 ppm ( $\text{CH}_3$ ). According to literature survey, the marked area 4.2 ppm was characterized glyceryl of triglycerides [43, 44].

$^1\text{H}$ NMR spectroscopy of biodiesel was done to characterize the protons in the sample (Fig. 4 B) which showed that the presence of similar peaks that observed in fig. 4A in addition to the presence of peak at 3.7 ppm which refer to the  $\alpha$ -carbonyl methylene groups ( $\text{OCH}_3$ ) and absence of peak at 2.1 ppm which refer to triglyceride ( $\text{CH}_2$ ) [45].

### 4. Conclusion

According to the study's findings, employing hexane as a solvent, the oil content of the Iraqi castor seed sample was 23.200 percent of its total weight. The prepared castor oil and its methyl ester were evaluated by study the chemophysical properties such as density, kinematic viscosity, refractive index, acid value, iodine and saponification values and compared with standard value which illustrated some differences between them So it can be concluded that the product of castor biodiesel wasn't have good agreement with the standard specification because of the presence of high quantity of ricinoleic acid (unsaturated acid) and it must be mixed with mineral oil or any other ester of fatty acid to make good agreement with ASTM specifications.







