



## Influence of chemical structure on physical properties of homogeneously converted (Castor-Linseed) mixed biofuel under optimized conditions



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### Abstract

In this study, different mixtures of castor oil and linseed oil were converted into their corresponding biofuel throughout homogeneous catalytic reaction using sodium hydroxide as homogeneous catalyst in the presence of methyl alcohol under optimized condition. The mechanism of the transesterification reaction of the oils was proposed. The physical properties of the obtained biodiesels were determined according to ASTM fuel specification. The results showed that the gradual increase in the abundance of castor oil in the oil mixture from 10% to 90% decreases the most of properties of the obtained biofuels to meet the standard values. The study presented a good sight into the preparation of biodiesels from various types of mixed vegetable oils.

*Keywords:* Transesterification; homogeneous catalyst; biofuel; physical properties.

### 1. Introduction

The present system for energy supply is responsible for various negative effects such as a high supply security risk, global and local environmental problems including: depletion of fossil resources, increase of greenhouse gases emission, acid rains and ozone layer depletion, and climate changes. These problems have motivated researchers and industrial sector to search and develop new energy resources and accessible cleaner technologies [1]. Over the last years, several possible fuels have emerged including compressed natural gas (CNG), liquefied petroleum gas (LPG), liquefied natural gas (LNG), methanol, ethanol, biodiesel (fatty acid methyl esters) [2]. Some of these options show clear evidence of environmental benefits on the complete fuel chain over petroleum fuels; however, some of these options exhibit a number of drawbacks that hinder their

ability to capture an important share of the market. These disadvantages include expensive technologies, vehicle modification, and separate distribution infrastructure, which require high investment and uncertainty in profit return [3]. Biofuels have a significant potential to overcome traditional barriers to entry into the market due to their compatibility with vehicles and blending tendencies with fossil fuels such as gasoline and diesel [4]. The conversion process of oils into biodiesel starts by the extraction of oil from the seeds. The process to produce fatty acid methyl esters from vegetable oils is a transesterification reaction with methanol. Transesterification reaction is characterized short time process, high conversion percentage, low cost catalyst, and comparatively low temperature required [5]. Catalytic cracking can be used also for producing alternative fuel liquids with comparative fuel properties using heterogeneous catalysts [6]. The catalytic cracking process is more costly than the transesterification process and the types of products

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are completely different. This study describes the conversion of castor oil-linseed oil mixture into biodiesel using sodium hydroxide as a catalyst in transesterification process, also the influence of the chemical structure of oils on the obtained mixed biofuel.

## 2. Materials and Methods

### 2.1. Extraction of oil

The linseed and castor seeds were sampled, dried, and then applied to hydraulic press to obtain the linseed oil (L) and castor oil (C). The oils were centrifuged to remove any solid contaminants and water, and used without further purification.

### 2.2. Preparation of biofuels using castor oil and linseed oil

The transesterification of castor oil with methanol was carried out at its optimized conditions following the procedure of Negm et al. [7]. The reaction was carried out in one litter three neck reaction flasks connected to a reflux condenser. The castor oil was mixed with methanol at a ratio of 6 mole alcohol/1 mole oil and the temperature was adjusted at 60 °C while stirring using magnetic stirrer at constant speed. Sodium methoxide was used as catalyst (2%) relative to castor oil. Progress of transesterification reaction was followed up during the process whereby samples were withdrawn over definite time intervals and tested using thin layer chromatography as to check for the time at which the reaction has been completed. The neutralization of the catalyst (sodium methoxide) was performed by diluted sulfuric acid using equivalent amount of used sodium methoxide. Transesterification of the obtained biofuel from *linseed* oil also was prepared in a similar method as in the case of castor oil with a methanol to oil ratio of 1:3.

### 2.3. Samples preparation

Castor oil (C) and linseed oil (L) used during the transesterification process were mixed in a different ratio; starting from 10% to 90% of castor oil, and the remainder is linseed oil to 100%. The obtained mixed biofuels were symbolized as: C1L9 for starting oil mixture contains 10% castor oil, and C9L1 for starting oil mixture contains 90% castor oil. The obtained biofuels were designated as MEC<sub>n</sub>L<sub>m</sub>, n, m: ratio of oils in the starting mixture.

### 2.4. Oil characterization

The fatty acid composition of (L) and (C) was determined using GC chromatographic analysis using GC-7890A instrument equipped with DB-23 column, 60 mm 0.25 mm, i.d. of 0.25 μm. The different properties of the oils were determined including: viscosity, density, sulfur content, pour point, cloud point, acid value, fatty acid composition, iodine value, saponification value, and oxidation stability.

### 2.5. Biofuel specification

The properties of EC, EL, MEC<sub>n</sub>L<sub>m</sub> were determined according to the standard test method [8]: viscosity (ASTM D-445), density (ASTM D-4052), carbon residue (ASTM D-189), ash content (ASTM D-4530), sulphate content (ASTM D-874), pour point (ASTM D-97), flash point (ASTM D-92).

## 3. Results and Discussion

### 3.1. Properties of Linseed oil and castor oil

The fatty acid compositions of linseed oil and castor oil were characterized and their values were comparable to the published data [9] with the abundance of unsaturated acids (oleic, linoleic and α-linolenic acids), and saturated fatty acids (palmitic and stearic acids). The properties of the two oils were determined and listed in **Table 1**. The influence of unsaturation sites of castor oil on its physical and chemical properties including density, oxidation stability, and viscosity, which were in higher values than linseed oil. That is due to the higher content of ricinoleic and linoleic acids in castor oil [10, 11].

**Table 1: Physicochemical properties of *linseed* oil and *Castor* oil**

Property	Test method	Castor oil	Linseed oil
Acid value, mg KOH/g	ASTM-D974	3.0	1.6
Viscosity at 40 °C, mm <sup>2</sup> /s	ASTM-D445	43.0	39.0
Density, kg/m <sup>3</sup>	ISO-3675	0.959	0.935
Pour point, °C	ASTM-D97	3	5
Oxidation stability, h	EN-14112	5.5	3
Iodine value, g I <sub>2</sub> /100 g oil	ISO-3961	80.5	177
Sulfur content	ASTM-D5453-93	0.05	0.05
Myristic acid (14:0)		----	0.1
Palmitic acid (16:0)		1.0	5.1
Palmitoleic acid (16:1)		----	0.1
Stearic acid (18:0)		-----	4.0
Oleic acid (18:1)		3.0	<u>17.4</u>
Linoleic acid (18:2)		5.0	<u>22.7</u>
Linolenic acid (18:3)		1.0	<u>50.0</u>
Arachidonic acid (20:0)		----	---
Ricinoleic acid 18:1(OH)		<b>89.0</b>	---

### 3.2. Properties of methyl ester *Castor* Oil (EC) and methyl ester *linseed* Oil (EL)

The chemical structures of the obtained biodiesels EC and EL were characterized using FTIR spectroscopy and compared with their parent oils (**Figure 1-2**). EC

and EL biodiesels showed characteristic absorption bands at:  $1742\text{ cm}^{-1}$  of ester carbonyl group;  $1460$ ,  $1436\text{ cm}^{-1}$  stretching of methoxy groups ( $-\text{OCH}_3$ ),  $1171\text{ cm}^{-1}$  stretching of  $\text{O}-\text{CH}_3$  group. These groups are the typical function groups in several fatty acid methyl esters of various vegetable oils [7, 12-13].

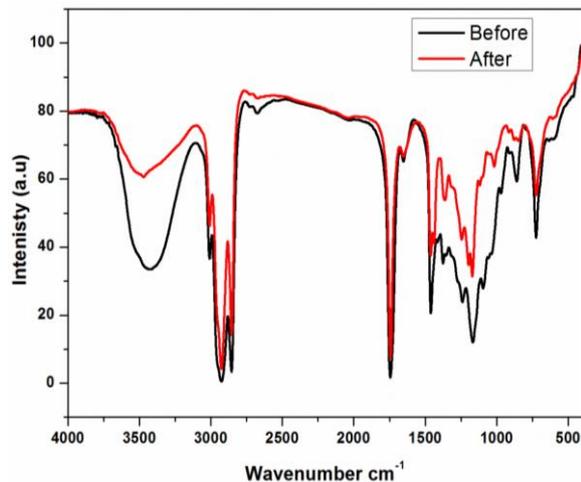


Figure 1: FTIR spectra of *castor* oil and biodiesel obtained from *Castor* oil.

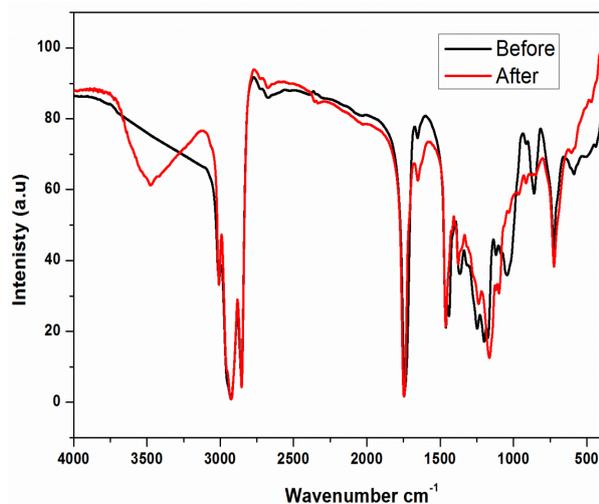


Figure 2: FTIR spectra of *linseed* oil and biodiesel obtained from *linseed* oil.

### 3.2.1. Density

The density of biodiesel is important character because it is related to the weight of the biodiesel in the engines [14]. Increasing the density increases the load on the engine, especially in cars. The obtained data of the densities of the pure biodiesels EL and EC were  $0.9289$  and  $0.9105\text{ g/cm}^3$ . The gradual increase in the ratio of C in the oil mixture of C:L is gradually decreases the recorded viscosity of the obtained

biodiesel (Figure 3). The decrease in the viscosity that accompanied by increasing C ratio in the mixture is attributed to the low value of the EC density. The data in Table 2 revealed that all the densities of the obtained biodiesels are located within the ASTM specification limits of  $0.860\text{-}0.930\text{ g/cm}^3$ .

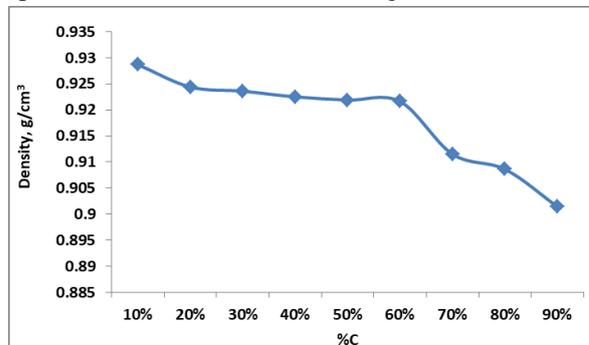


Figure 3: Variation of density of the obtained biofuel by changing the biofuel of castor oil ratio.

### 3.2.2. Viscosity

The viscosity of the fuel represents the degree of fluidity of the fuel in the tubes and in the circulating system of the engine. It is an important characteristic due to high viscosity fuel will requires pumping into the ignition or compression chambers of the various engines. The viscosities of EL and EC were  $3.59$  and  $4.63\text{ cSt}$  (Table 2). The high viscosity of EC can be attributed to the presence of branched ethoxy groups, which formed by the reaction of the methyl alcohol with the hydroxyl groups, in addition to the unreacted hydroxyl groups within the ricinoleate chains in C oil. EL has lower viscosity due to the homogeneous straight chain of its fatty acids. The viscosities of the obtained biofuels after the transesterification reaction of L and C were increased gradually by increasing the ratio of C in the oil mixture (Table 2) to reach its maximum value at  $4.53\text{ cSt}$  for MEC9L1 biodiesel.

### 3.2.3. Boiling point

Boiling point of biodiesel determines the point, at which it begins to boil, i.e., the change from liquid phase to vapour phase. This point is very important because it determines the ability to transport and save biodiesel at thermal condition. Low boiling point fuels cause problems during transportation due to the ability of ignition and forming vapours with critical fuel concentration. The boiling points values of EL and EC were  $178$ , and  $153\text{ }^\circ\text{C}$ , respectively. The obtained temperatures are in good agreement with the reported values [15]. It is clear that the gradual increase in the ratio of C in the mixed oil to  $40\%$ , i.e.,

MEC4L6, the boiling points of the obtained biodiesels were higher than EC boiling point. But, the gradual increase in C ratio in the mixed oil than 40% reduced the boiling points of the obtained biodiesels to 149 °C for MEC5L5, and 122 °C for MEC9L1 (Figure 4). The presence of unsaturation in the chemical structure of the fatty acids of the oils increases the boiling points of their corresponding biodiesels [16]. The obtained boiling points of the different biodiesel were located within the range of the standard specification of ASTM limits.

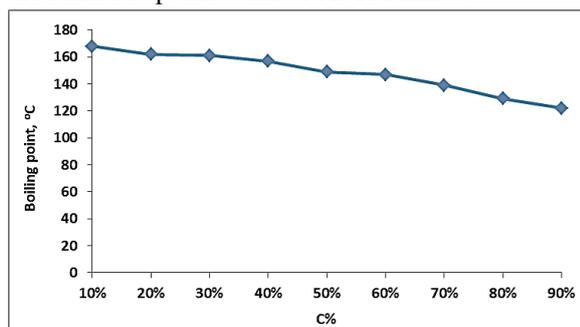


Figure 4: Variation of boiling point of the prepared biofuels at varied ratios of C.

### 3.2.4. Pour point

The pour points of both EC and EL were determined and found at -9, -11 °C, respectively, and these values were in accordance with the reported data [17]. The pour points of the different biodiesel mixtures were varied between -11 °C and -8 °C, Table 2. It is clear from Table 2 that the gradual increase in L content in the oil mixture is gradually decreases the pour point of the obtained biofuels. The higher content of EL biodiesel (MEC1L9) has the lowest pour point at -11 °C, while the higher EC content in the biodiesel (MEC9L1) has the highest pour point of -8 °C. The higher unsaturated fatty acid methyl esters have lower pour points than those of lower unsaturated chains [18]. The pour points of the obtained biodiesels were ranged between -11 and -8 °C, which were located in the acceptable range of biodiesel ASTM specifications [8]. As represented from the obtained data in Table 1, it is favourable to produce biodiesels from oil mixtures which contain more unsaturated oils than the saturated oils.

Table 2: Physical and fuel properties of the pure EC and EL biofuels and the mixed biofuels (MECnLm)

Biofuel Formula	Density 15.6 C°	Viscosity 40 C°	LB.P	Pour Point	Fire Point	Smoke Point
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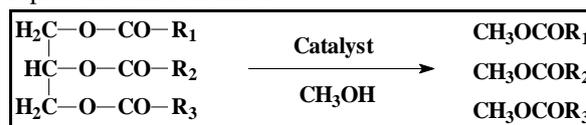
MEL10	0.9289	3.59	178	-11	99	41
MEC1L9	0.9287	3.69	168	-11	96	39
MEC2L8	0.9244	3.80	162	-11	95	39
MEC3L7	0.9236	3.90	161	-10	95	39
MEC4L6	0.9225	4.01	157	-10	92	38
MEC5L5	0.9219	4.11	149	-9	92	38
MEC6L4	0.9216	4.21	147	-8	90	37
MEC7L3	0.9115	4.32	139	-8	89	37
MEC8L2	0.9086	4.42	129	-8	88	37
MEC9L1	0.9014	4.53	122	-8	88	37
MEC10	0.9105	4.63	153	-9	95	38

### 3.2.5. Fire and smoke points

The fire point reflects the condition at which vapour burns, while the smoke point is the temperature at which the fuel starts to burn and smoke. The smoke point, also referred to as the burning point, is the temperature at which fuel begins to produce a continuous bluish smoke that becomes clearly visible, dependent upon specific and defined conditions. The fire points of the obtained pure biodiesels EL and EC were 99, 95 °C. The gradual increase in the percentage of C in the mixed oils has a gradual decreasing influence on the fire and smoke points of the obtained biodiesels Table 2. That can be attributed to the differences in the chemical structures of the fatty acid moieties incorporated in the structure of the different triglycerides (oils).

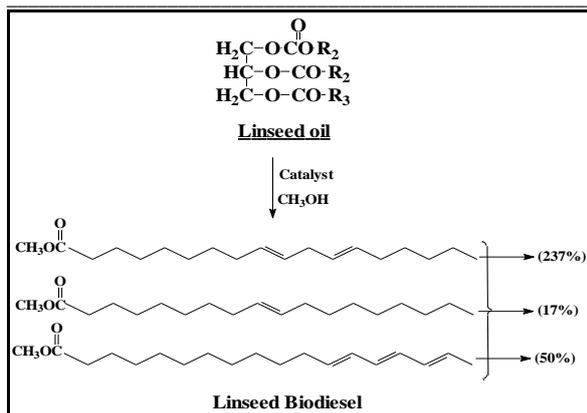
### 3.3. Transesterification Mechanism

Vegetable oils (triglycerides) are esters of saturated and unsaturated monocarboxylic acids with glycerol, which react with alcohol in the presence of catalysts (transesterification) to produce the biodiesel. Biodiesel is methyl esters of different fatty acids of vegetable oils, formed in a typical reaction represented in Scheme 1.



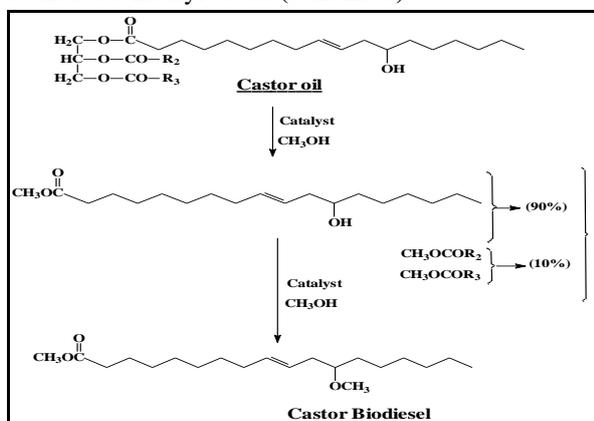
Scheme 1: Transesterification process of vegetable oils into biodiesel.

The transesterification reaction includes hydrolysis of the ester groups formed between the glycerol and the different fatty acids and formation of new ester bonds between methanol and the different fatty acids. One trihydric alcohol with three hydroxyl groups (glycerol) is replaced by three equivalent monohydric alcohols with one hydroxyl group (methanol). This can explain the molar ratio of *castor* oil and *linseed* oil to methanol molar ratio at optimized conditions of the transesterification reaction at 1:6 (Scheme 2).



**Scheme 2: Transesterification process of *linseed* oil into its corresponding biodiesel.**

FTIR spectra of the *linseed* oil and its biodiesel were similar to each other. This is due to the formed function groups in the obtained biodiesel are similar to those in the *linseed* oil (**Figure 2**). In case of *castor* oil, the chemical structure of the fatty acids in the *castor* oil plays an important role in the oil conversion into biodiesel. Due to the high presence of ricinoleic acid in (90%), the reaction by methanol occurred at two centres. The first is the transesterification reaction of *castor* oil to form its corresponding methyl esters, the second is the etherification of the hydroxyl groups of the ricinoleate moieties to form methyl substituted ricinoleate methyl esters (**Scheme 3**).



**Scheme 3: Transesterification process of *castor* oil into its corresponding biodiesel.**

FTIR spectra of *castor* oil represent a new band appeared at  $1050\text{ cm}^{-1}$  corresponds to the ether bond formation between the hydroxyl groups of the ricinoleate moiety and the ethanol ( $\text{C}-\text{O}-\text{CH}_3$ ) (**Figure 1**). That proves the supposed two reaction steps of *castor* oil conversion to biodiesel as represented in **Scheme 3**. The proposed mechanism of transesterification reaction of *castor* oil explains

the *castor* oil to methanol higher molar ratio. That is due to the participation of methanol in two considerable reactions, i.e., transesterification and etherification reactions, which incorporated in each reaction by approximately equal amount, and consequently to optimize the molar ratio, it must be double of that required in case of conversion of *linseed* oil to biodiesel.

#### 4. Conclusion

From the results of the study, the mixed oils can be used to produce biodiesels with high performance and in good agreement with the standard specification in case of the presence of high content of unsaturated oil in the oil mixture.

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