

## BIODIESEL- A TRANSESTERIFIED PRODUCT OF NON-EDIBLE CASTOR OIL\*\*

Muhammad TARIQ,<sup>a,\*</sup> Ahmad Kaleem QURESHI,<sup>b,\*</sup> Muhammad IMRAN,<sup>b</sup> Muhammad Babar TAJ,<sup>b</sup>  
Muhammad SIRAJUDDIN,<sup>c</sup> Saqib ALI<sup>d</sup> and Naseem ABBAS<sup>a</sup>

<sup>a</sup>Institute of Chemical Sciences, Bahauddin Zakariya University, 60000, Multan, Pakistan

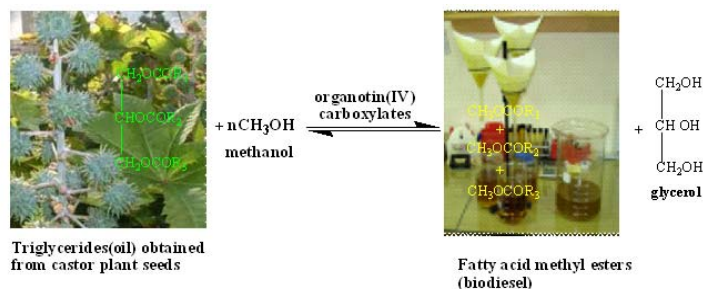
<sup>b</sup>Department of Chemistry, The Islamia University of Bahawalpur, 63100, Bahawalpur, Pakistan

<sup>c</sup>Department of Chemistry, University of Science & Technology, 28100 Bannu, Pakistan

<sup>d</sup>Department of Chemistry, Quaid-i-Azam University, 45320, Islamabad, Pakistan

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The use of base (KOH, NaOH etc.) for transesterification of oil has many demerits. So, in this study the transesterification of castor oil has been carried out in the presence of organotin(IV) carboxylates [ $R_2SnL_2$ ,  $R = CH_3$ - (1),  $n-C_4H_9$ - (2)] and [ $R_3SnL$ ,  $R = CH_3$ - (3),  $n-C_4H_9$ - (4),  $C_6H_5$ - (5)],  $L = 3$ -(4-fluorophenyl) acrylic acid]. The percentage conversion of triglycerides in castor oil into fatty acid methyl esters (biodiesel) was determined by  $^1H$  (Proton) NMR. The results showed that the triorganotin(IV) compounds exhibited good catalytic activity than their di-analogues. The physical and fuel properties of the synthesized castor oil biodiesel like density, kinematic viscosity, pour point, cloud point, flash point and acid number were determined by ASTM methods. The density, flash point and acid number are in accordance to ASTM values but kinematic viscosity value is a bit higher due to more viscous and denser parent oil. The pour point and cloud point values are lower than ASTM values which are beneficial for the highly cold weather conditions.



### INTRODUCTION

The paucity of petroleum goods generated curiosity in exploring diverse substitute fuel sources, like solar, biofuel (bio-diesel or ethanol), biomass etc. Bio-diesel got a key significance for the previous 16 years as the prime viable substitute of diesel. It may be utilized in automobiles in pure form B100 or mixed B5, B10, B20. From a chemistry point of view, bio-diesel contained methyl esters of fatty acid that are synthesized from edible or non-edible vegetable oil or animal fats or waste cooking oil through transesterification

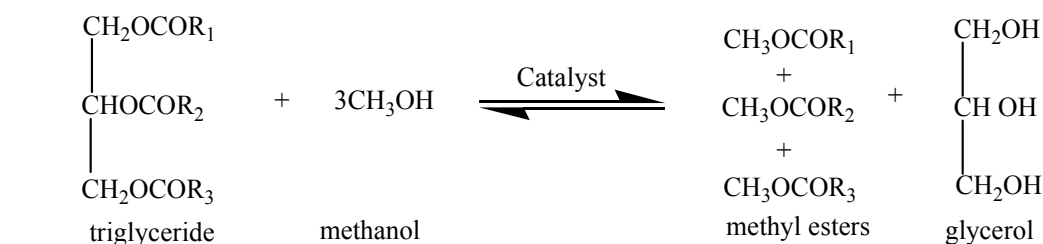
process.<sup>1-3</sup> The usage of bio-diesel fuel can extend the life of the diesel engine due to more greasing power and power outputs are relatively unaffected. Its use is also environmentally friendly as it produces less emission of CO, HCs, particulate matter, SO<sub>2</sub> and VOCs.<sup>4</sup>

Scientists have been working on the production of biodiesel from vegetable oil due to a possible future deficiency of petroleum diesel.<sup>5-10</sup> The FAMEs have been obtained from various oil sources like rapeseed, soybean, sunflower, palm, rocket seed oil<sup>11-15</sup> utilizing sodium hydroxide or potassium hydroxide catalyzed transesterification.

\* Corresponding authors: ak.queshi@iub.edu.pk; drtariq2013@hotmail.com

\*\* Supplementary information on <http://web.icf.ro/rrch/> or <http://revroum.lew.ro/>

But basic catalysts have disadvantages like plenty of washing, soap formation and need for less free fatty acids containing oils (edible oils). Another option is use of acid homogeneous catalysts like sulphuric acid, phosphoric acid, hydrochloric acid, organic sulphonic acid etc. for high FFA precursor oil adopting both esterification and transesterification. But their use is limited due to requirement of high methanol to oil ratio, temperature, pressure adjustment and high amount of catalysts concentration.<sup>16-20</sup> An additional class of catalysts is heterogeneous catalysts which are further classified into solid base heterogeneous and solid acid heterogeneous catalysts.<sup>21-25</sup> The heterogeneous catalysts can be easily separated, and recycled/ reused. The solid base heterogeneous catalysts include metal oxides e.g. CaO, MgO, ZnO, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SrO, WO<sub>3</sub>/ZrO<sub>2</sub>, Mg-Al hydrotalcites, sulphated SnO, sulphated zirconia oxide, clay minerals and non-oxides.<sup>26</sup> However the use of these solid base catalysts have been reported demerits like requirement of low free fatty acid (FFA) feedstock because soap formation decrease percentage yield of biodiesel.<sup>26,27</sup> The solid acid heterogeneous catalysts include tungstated sulphated zirconia, ion-exchange resin, zeolites and metal complexes which have disadvantages of long reaction time, high ratio of alcohol (methanol), high temperature and pressure, low acid sites, and poisoning of the catalysts etc.<sup>26,27</sup> To the best of our knowledge, there is limited literature on use of metal complexes especially tin(IV) metal complexes in transesterification of triglycerides to produce fatty acid methyl esters. So by keeping in view, the literature, in the present study, castor biodiesel was synthesized by tin (IV) metal complexes catalyzed transesterification.



#### Fuel properties of castor biodiesel

The fuel properties of synthesized bio-diesel like density, kinematic viscosity, cloud point (CP), pour point (PP) and flash point (FP) were determined using ASTM standards. These parameters were found out and compared with ASTM methods. The findings are given in Table 1

## EXPERIMENTAL

The seeds were obtained from the market. To remove dirt, the seeds were washed with water and then dried in an oven at 60°C. German made electric oil expeller (KEK P0015-10127) was used to extract oil. MeOH, NaOH and anhydrous Na<sub>2</sub>SO<sub>4</sub> were purchased from Merck (Germany). The synthesis and complete characterization of organotin(IV) compounds which were used as catalysts in this study were reported in our previous work<sup>28</sup> and chemical structures are given in the form of table in supplementary material (S1 Table). For transesterification reaction, the methanol (0.04 mol, 1.282 g), castor oil (0.01 mol, 8.9 g) and tin compound (0.1 mmol) in methanol/oil /catalyst ratio of 400:100:1 were added in three neck round bottom flask connected with reflux condenser, thermometer and refluxed at 65 °C with constant stirring as described by Abreu F. R. *et al.*<sup>5</sup> Before the reaction, tin compounds were made soluble in CHCl<sub>3</sub>. The sample was taken out after every 08 hours. <sup>1</sup>HNMR was done to find out percentage conversion of TGs into FAMES.

The fuel parameters of synthesized castor biodiesel were found by ASTM methods in Hydrocarbon Laboratory using standard apparatus like Viscometer VI-9730-945, density meter SBS-3500, Flashpoint tester Pensky Martens Closed Cup BTFT-3, Pour point detector FG-KI-400-KW and Cloud point detector FG-K 12663-KW. Castor biodiesel can be identified by the FTS3000MX infrared spectrometer in the mid-infrared range. NMR analyses were done using Avan CE 300 MHz spectrometers. TMS was used as an internal standard while CDCl<sub>3</sub> as a solvent. The FAMES composition of synthesized bio-diesel were found out by GC, model GC-6890N connected with MS, model MS-5973 MSD. Partition was done on a capillary column DB-5MS (30 m × 0.32 mm, 0.25µm of film thickness). The MS was set to scan in the range of m/z 50-550 with EI ionization mode.

## RESULTS AND DISCUSSION

Bio-diesel was synthesized from the castor oil utilizing NaOH and tin compounds. The transesterification reaction is represented as:

and explained as follows:

#### Density (g/cm<sup>3</sup>):

The density of castor oil is 0.961 g/cm<sup>3</sup> which is reduced to 0.921 after transesterification but little bit more to ASTM standards (0.90 g/cm<sup>3</sup>). The density can be made equivalent to ASTM standards by making blend with diesel fuel.

Table 1

Fuel parameters of synthesized biodiesel

PARAMETERS	ASTM STANDARD	ASTM STANDARD	ASTM STANDARD	SYNTHESIZED CASTOR BIO-DIESEL	CASTOR OIL
		Petrodiesel	Biodiesel		
D (15°C, G CM <sup>-3</sup> )	D 5002	0.834	0.86-0.90	0.921	<b>0.961</b>
K.V (40°C, MM <sup>2</sup> S <sup>-1</sup> )	D 445	1.9-4.1	1.9-6.0	15.59	<b>240</b>
C P (°C)	D 2500	-15 to 5	-3.0 to 12	-14.0	-
P.P (°C)	D 97	-35 to -15	-15 to 16	-19.1	-
FP (°C)	D 93	60-80	100 to 170	186	<b>229</b>
ACID NUMBER (MG KOH G <sup>-1</sup> )	—	<b>0.5</b>	<b>0.5</b>	<b>0.85</b>	<b>1.148</b>

**Kinematic viscosity (mm<sup>2</sup> s<sup>-1</sup>):**

The kinematic viscosity of castor oil is 240 mm<sup>2</sup> s<sup>-1</sup> which is reduced to 15.59 mm<sup>2</sup> s<sup>-1</sup> after transesterification but more than ASTM standards. However, viscosity can be decreased by making blends with diesel fuel as B10, B20 but B100 cannot be used in diesel ignition engine.

**Pour point (PP) and cloud point (CP):**

The PP is the minimum temperature at which the fuel can stream while CP represents first visibility of wax in the fuel in cold weather. At low temperature, especially in cold weather conditions, the use of biodiesel and diesel cause restriction in flow leading to obstruct the fuel lines and filters. However, castor oil biodiesel showed little bit different trend as the find out figures of CP and PP of synthesized biodiesel were -14 and -19.1°C, respectively which are very low as compare to ASTM standards. But these low values make it very much suitable in cold weather conditions.

**Flash point (FP):**

Flashpoint (FP) is the temperature-representing ignition of fuel when bare to a spark or flame. The flash point of castor oil is 229°C which is reduced to 186°C in castor oil biodiesel obtained after transesterification. However, this value is still slightly higher than ASTM standard maximum value of 170°C but can be made low by making various types of mixture blend with diesel. Although the higher flash point of biodiesel makes it more safe with respect to storage and handling but this benefit is countered with difficulty in combustion in starting the vehicle.

**Acid Number:**

The acid value accounts for presence of free fatty acids. The acid value of castor oil is 1.148 mg KOH/g which is reduced to 0.85 mg KOH/g in

castor oil biodiesel. This value is higher than ASTM standard value of 0.5 mg KOH/g because of presence of more free fatty acids.

Castor oil is denser and more viscous oil. Therefore after conversion into biodiesel, its various properties do not meet 100 % with ASTM standards but little bit more than ASTM standards. However these properties are decreased as compared to parent castor oil after transesterification and our results are better than Sreenivas *et al.*<sup>29</sup>

**FT-IR study**

The synthesized bio-diesel was analyzed using infrared spectrophotometer to have an idea about synthesis via appearance and disappearance of vibrational bands at specific wavenumber. The FT-IR spectrum of castor biodiesel is represented in Figure 1 and FT-IR data of important vibrational bands is given in Table S2(supplementary material). The methoxy C=O peak observed at 1741 cm<sup>-1</sup>. The overtones of ester group were observed as a wide band at 3465 cm<sup>-1</sup>.<sup>19,20</sup> The two asymmetric bands at 1171 and 1017 cm<sup>-1</sup> were attributed to C-O. The bands at 2924, 2854 and 3007 cm<sup>-1</sup> show CH<sub>3</sub>, CH<sub>2</sub> and CH groups, respectively. The bands at 1436 and 1361 cm<sup>-1</sup> denote bending vibrations of a methyl group and bands at 724 cm<sup>-1</sup> and 1245 cm<sup>-1</sup> denote bending vibrations of methylene group.<sup>7,30-33</sup>

**Multinuclear (<sup>13</sup>C and <sup>1</sup>H) NMR study**

The <sup>1</sup>H NMR of castor oil and its synthesized biodiesel are shown in Figure 2 and 3(a and b), respectively. The oil mainly consists of triglycerides while biodiesel consists of fatty acid methyl esters. The glyceridic protons (backbone of triglyceride molecule) signal was observed at 4.12-

4.33 ppm as shown in  $^1\text{H}$  NMR of castor oil in Figure 2.  $\text{CH}_3\text{O}$  (methoxy) signal was observed at 3.57 ppm (Figure 3a) and 3.65 ppm (Figure 3b) and  $\alpha\text{-CH}_2$  triplet at 2.19 ppm (Figure 3a) and 2.26 (Figure 3b), respectively. The methoxy protons signal represent the formation of FAMEs. This signal was not present in the oil. The absence of glyceridic protons signals while emergence of methoxy protons signal confirm the conversion of triglyceride into fatty acid methyl ester. The signals at 0.78, 1.18, 1.51 and 5.24 ppm (Figure 3a) and 0.87, 1.26, 1.97 and 5.28 ppm (Figure 3b) indicate terminal methyl, methylene,  $\beta$ -carbonyl protons and olefinic protons, respectively.<sup>34-36</sup> The percentage conversion of oil to FAMEs was found out by  $^1\text{H}$  NMR using the following formula.<sup>37, 38</sup>

$$C = 100 \times \frac{2A_{\text{Me}}}{3A_{\text{CH}_2}}$$

C= Conversion,  $A_{\text{Me}}$ = integration value of methoxy protons,  $A_{\text{CH}_2}$ = integration value of  $\alpha$ -methylene protons.

The percentage conversion of TGs to corresponding FAMEs using organotin(IV) compounds were represented in Figure 4. The Figure 4 shows that all the tested organotin(IV) complexes showed catalytic activity in transesterification reaction, however  $\text{Me}_3\text{SnL}$

showed maximum conversion up to 85 % in 24 hr reaction time (Figure 3b). The triorganotin(IV) complexes exhibited comparatively more percentage conversion than their di-analogues which may be due to their structural property. The triorganotin(IV) complexes being lesser in size than di-analogues that make attack easier on bulky triglycerides molecules. Glycerol is the other main product obtained along with fatty acid methyl esters. As the conversion is not 100 %, some other products may be unreacted monoglycerides, diglycerides, triglycerides and free fatty acids. The selection of tin complexes was due to Lewis acid and co-ordination expansion property of Sn centre. These properties may play vital role in the catalytic conversion of triglycerides into fatty acid methyl esters. The proposed mechanism has been given in supplementary material (S3). The tin atom causes activation of carbonyl groups in triglycerides by increasing the electrophilicity of the carbonyl carbon. The use of these catalysts in transesterification of triglycerides in oil to produce fatty acid methyl esters in biodiesel is quite better because of reduction of length of time of water washing, neutralization steps to separate, recovery of the used catalyst and insensitivity to FFA. However, the rate of reaction is slower and having a possibility of unwanted side reactions.

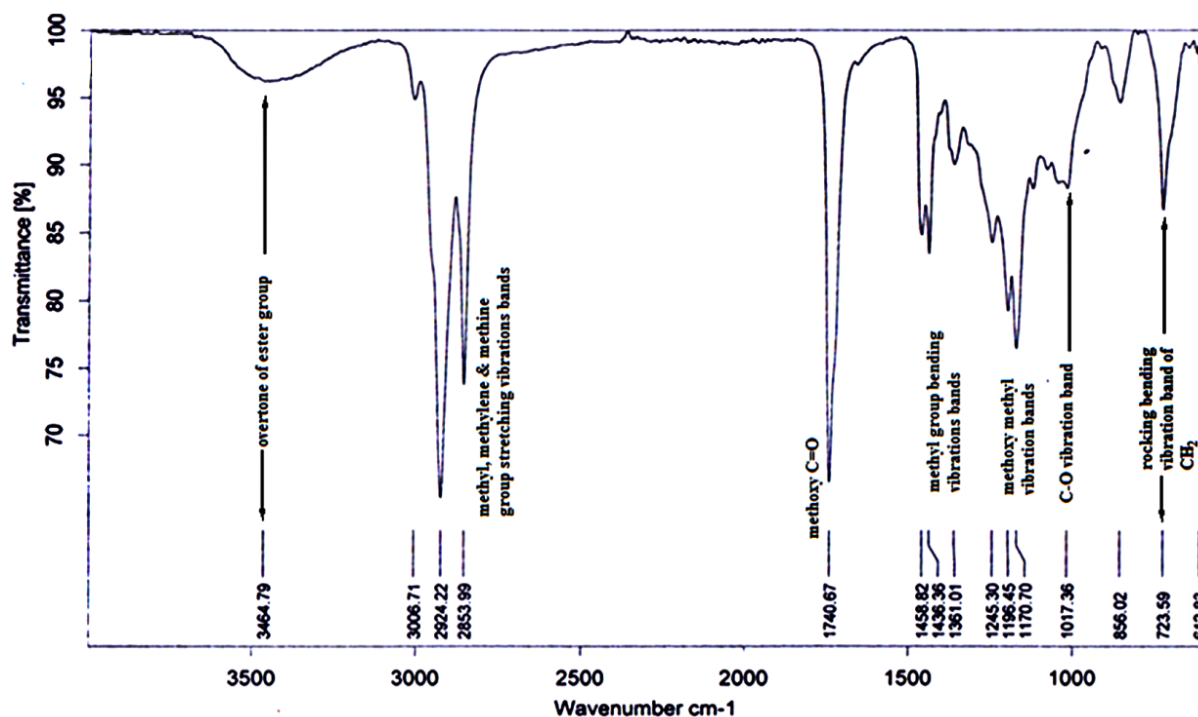


Fig. 1 – FT-IR spectrum of castor biodiesel.

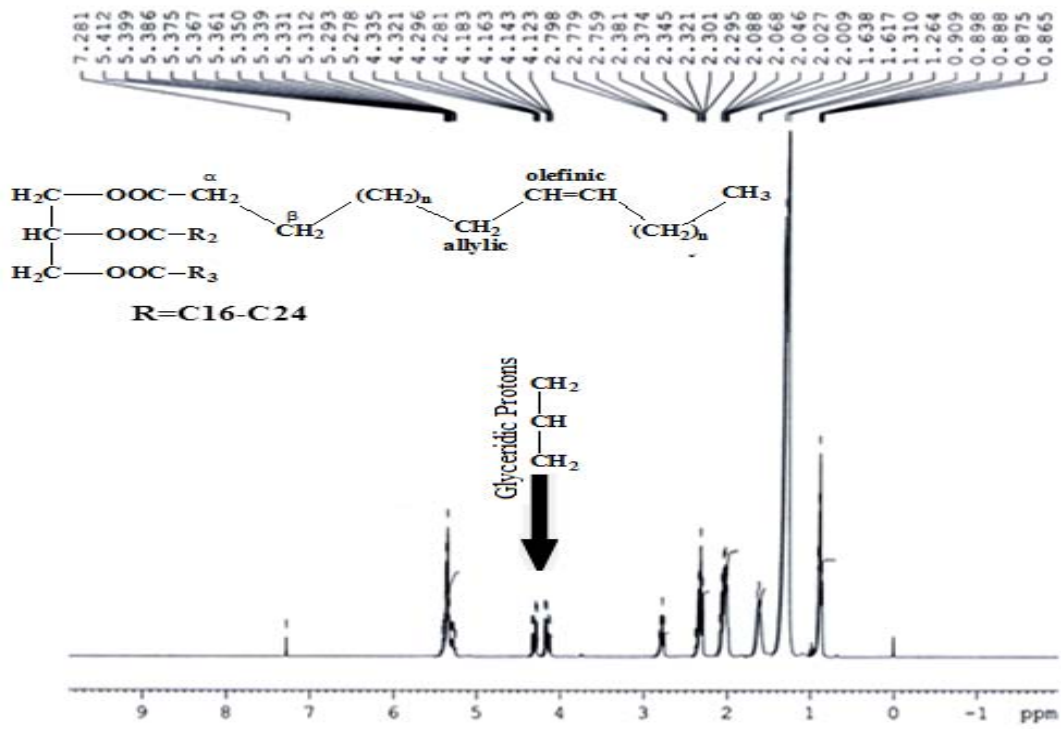


Fig. 2 – <sup>1</sup>H NMR spectrum of castor oil.

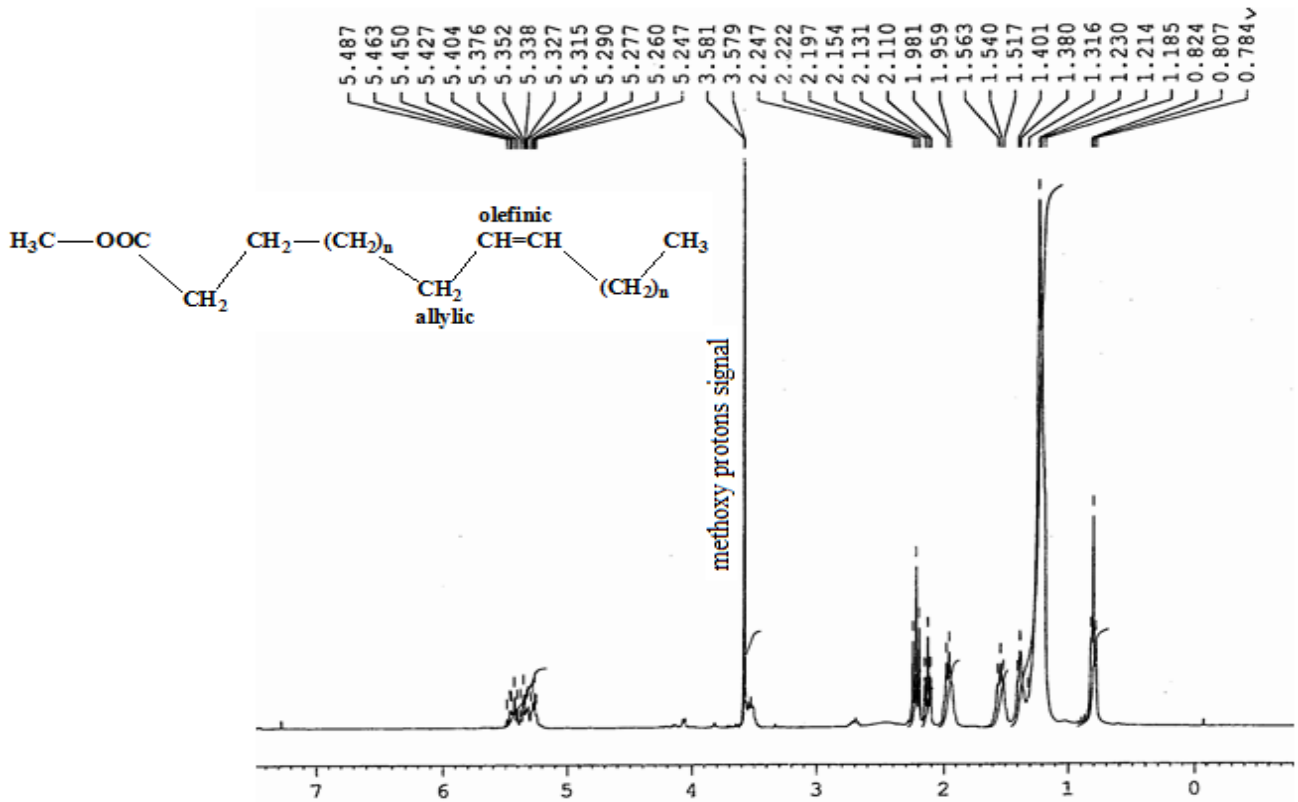


Fig. 3a – <sup>1</sup>H NMR spectrum of castor biodiesel by NaOH as catalyst.

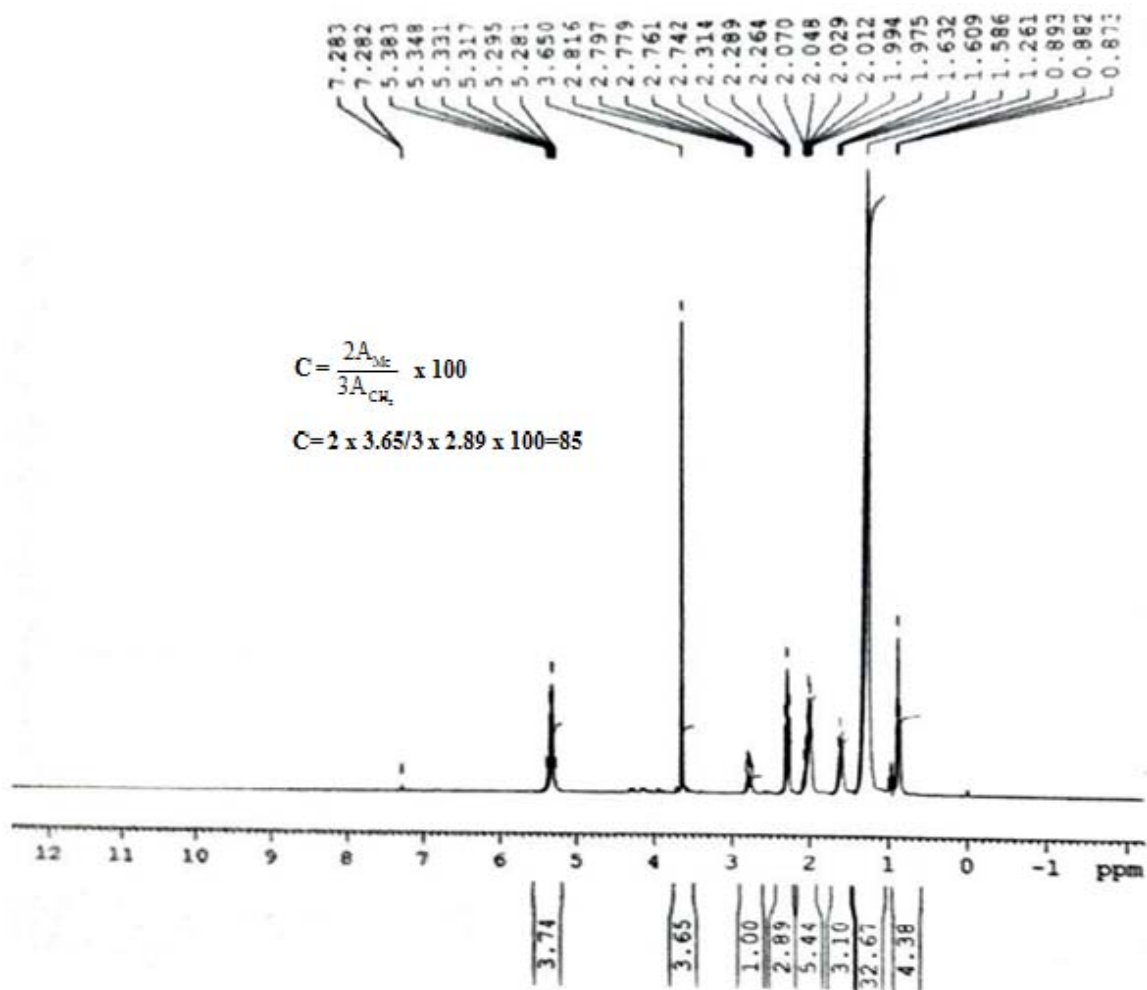


Fig. 3b –  $^1\text{H}$  NMR spectrum of castor biodiesel by  $\text{Me}_3\text{SnL}$  as catalyst.

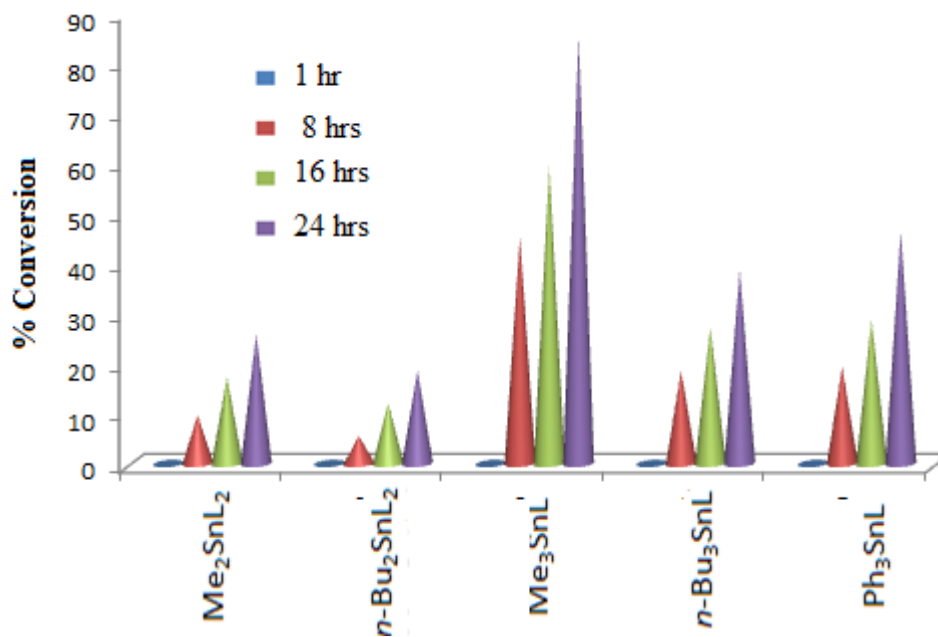


Fig. 4 – Percentage conversion of triglycerides into FAMES.

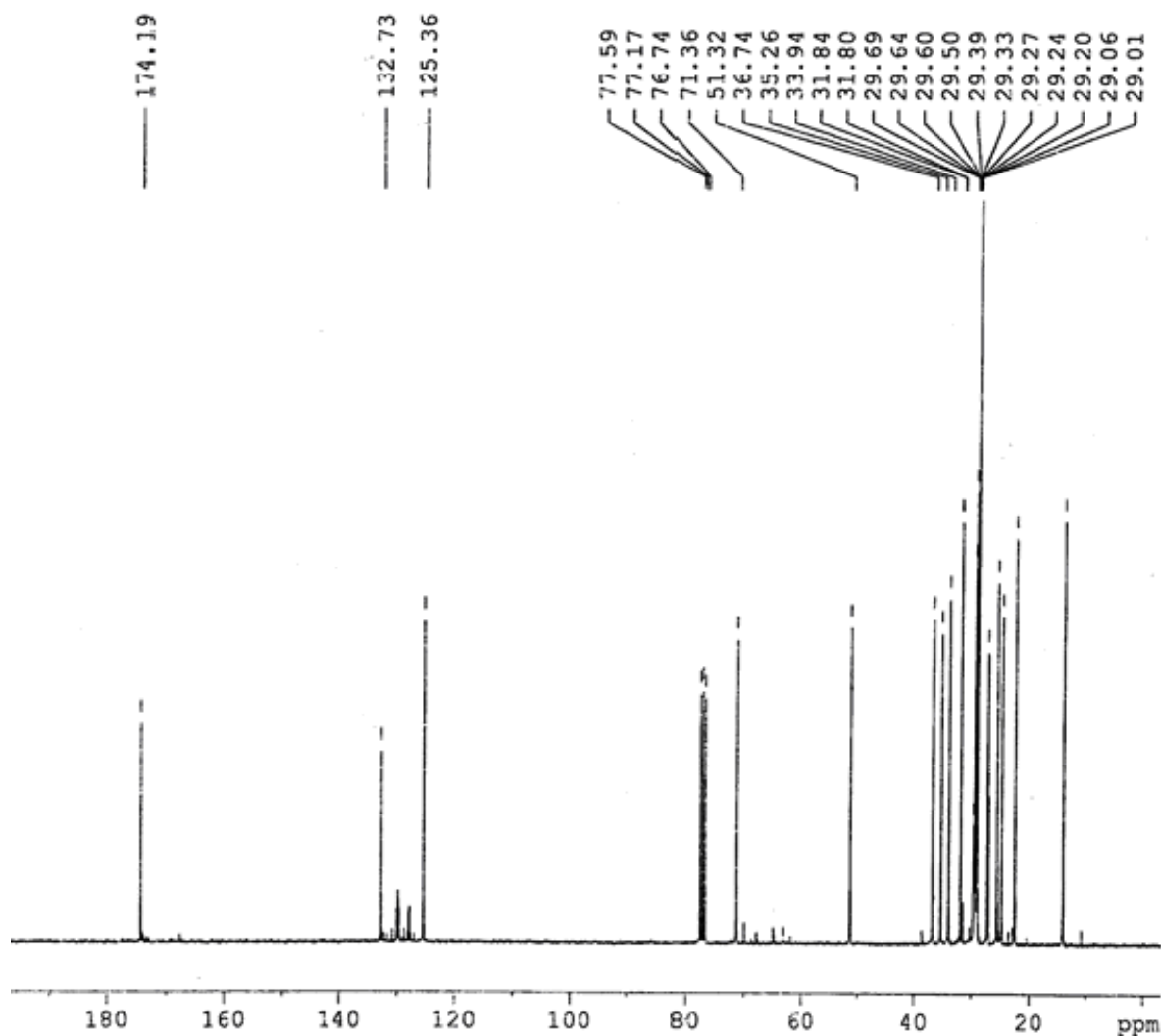


Fig. 5 –  $^{13}\text{C}$  NMR spectrum of castor biodiesel.

$^{13}\text{C}$  NMR spectrum of the castor biodiesel (Figure 5) showed the main peaks of ester carbonyl ( $-\text{COO}-$ ) and C-O at 174.19 and 51.32 ppm, respectively. The peaks from at 125.36, 132.73 ppm exhibited the unsaturation in methyl esters whereas the peaks at 76.74–77.59 ppm are related to chloroform carbon used as a solvent. Other peaks at 13.96–14.00 ppm are allocated to methyl terminal carbon and signals at 29.01–36.74 ppm is related to methylene carbons of long carbon chain in FAMES.

#### Gas chromatographic and mass spectrometric analysis

The fatty acids composition of synthesized biodiesel was found out by GC-MS. The total ion chromatogram (Figure 6a) show seven major peaks of FAMES at various retention times which were

identified using the standard matching MS library (NO. NIST 02) and mass fragmentation pattern.<sup>7,39</sup> Three saturated and four unsaturated FAMES were recognized in GC-MS analysis. The identified FAMES with carbon chain length and number of unsaturated bond (represented in small brackets) are shown in Figure 6b. Castor biodiesel is distinguished by its monounsaturated hydroxy content of ricinoleic acid, methyl ester (C18:1) with 89.7 % composition while other fatty acid methyl esters are present in very small concentration.

#### Effect of catalyst concentration on percentage conversion of biodiesel

The effect of catalyst concentration was checked on transesterification by selecting one organotin(IV) catalyst which gave the highest

percentage conversion described in the results and discussion section. The concentration of trimethyltin(IV) 3-(4-fluorophenyl) acrylate was varied from 0.1 to 0.5 millimole. The results are shown in Figure 7. The results showed that by increasing catalyst concentration, percentage conversion increases up to a certain limit. Further

increase in catalyst concentration causes a decrease in percentage conversion which may be due to the solubility problem of the catalyst because the catalyst is slightly soluble in methanol and made soluble in chloroform before the reaction as mentioned in experimental section.

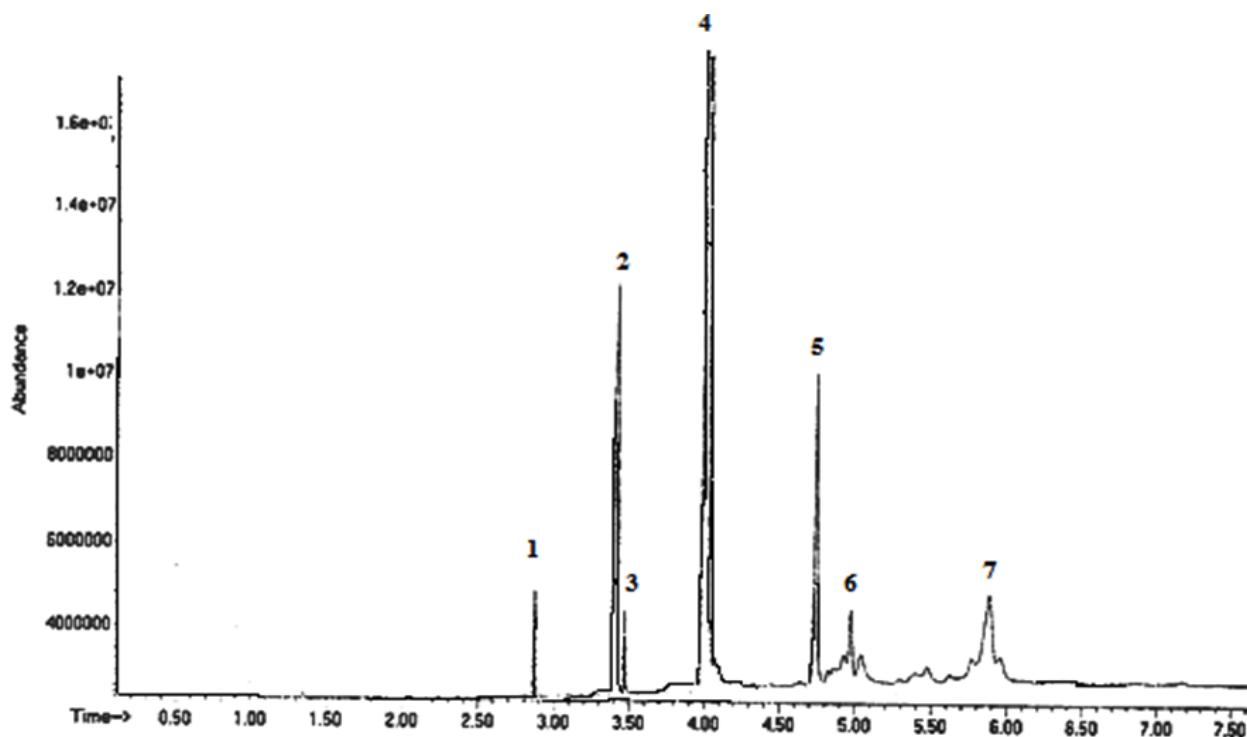


Fig. 6a – Total ion chromatogram of castor biodiesel.

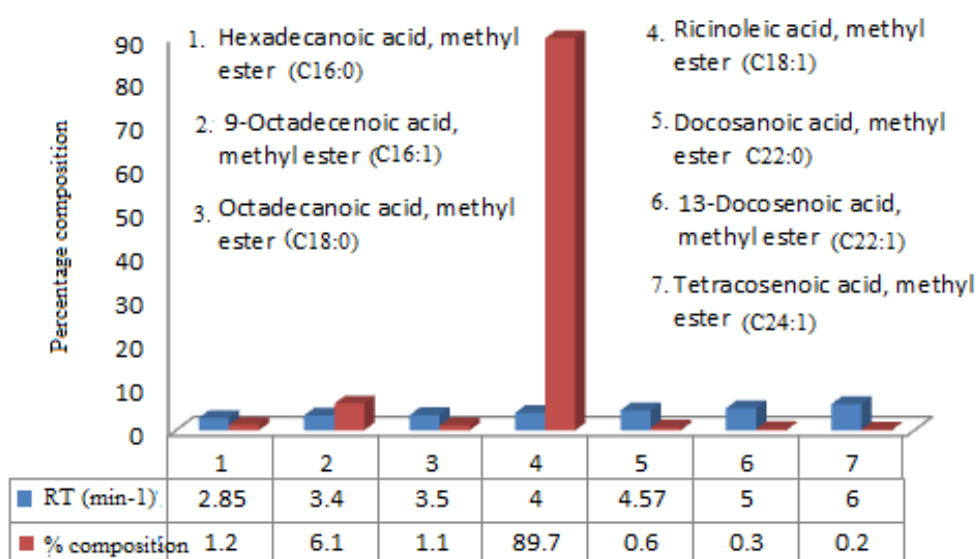


Fig. 6b – Identified FAMES at various retention time and composition in castor biodiesel.



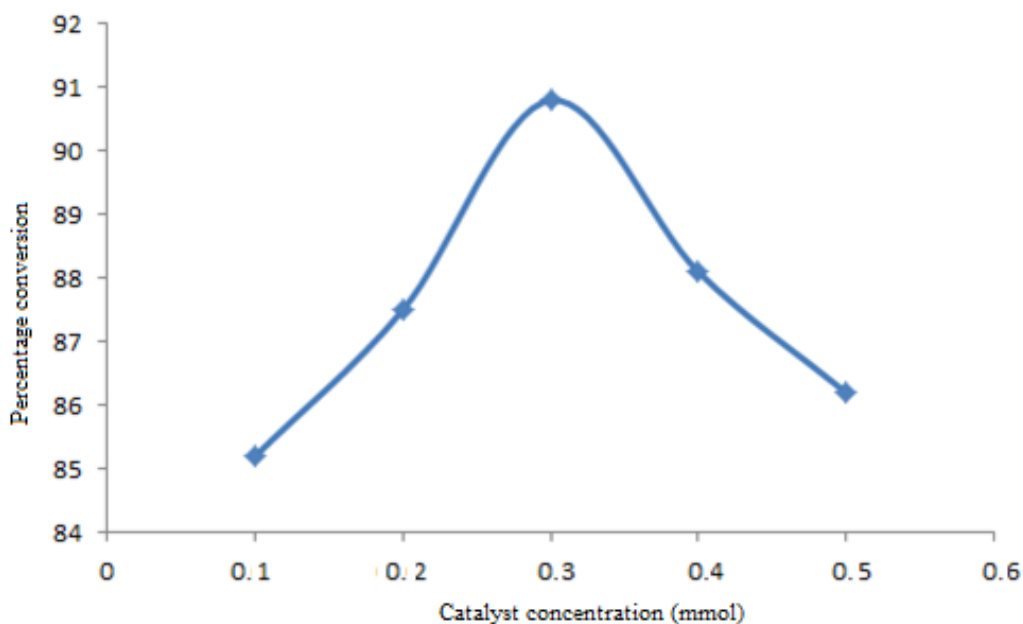


Fig. 7 – Effect of catalyst concentration on percentage conversion.

## CONCLUSION

The transesterification of castor seed oil with methanol to produce biodiesel was successfully performed using organotin(IV) complexes as catalysts. The organotin(IV) complexes gave variable percentage conversion up to 85 %. Out of them, trimethyltin(IV) 3-(4-fluorophenyl) acrylate produce 85 % maximum conversion in 24 h. The determined fuel properties like density, kinematic viscosity, flash point and acid value are little bit higher than ASTM limits so it is recommended to make blend like B10, B20 or B50 with diesel fuel to make these properties comparable to ASTM standards. However, the CP and PP are very lower than ASTM standards which is a advantage in one way to be used in cold weather conditions. The castor biodiesel was characterized by FT-IR and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) analyses. The chemical composition of methyl esters were determined by GC-MS. Seven fatty acid methyl esters were identified in castor biodiesel ranging from C16 to C24 by chromatographic retention time data and verified by mass fragmentation pattern. The effect of catalyst concentration on percentage conversion of triglycerides to FAMES was also checked for one catalyst (i.e.  $\text{Me}_3\text{SnL}$ ) that gave better percentage conversion.

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