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Research Article

Catalytic Conversion of Castor Oil into Biodiesel by Tri-organotin(IV) Catalysts: Chromatographic and Spectroscopic Characterization with Theoretical Support

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Abstract: Economic concern over fossil fuel reserves, extensive increase in CO_2 emission, and change in the world climate due to the combustion of carbon sources have been driving the attention of both commercial and academic researchers towards new sustainable fuel routes to encounter rapidly growing worldwide population demands. In the present study, we have focused on catalytic transesterification towards the environmentally friendly biodiesel synthesis which is low cost, easily implemented and best alternative source of fossil fuels. Herein three triorganotin(IV) carboxylates derivatives namely trimethylstannyl cyclopentanecarboxylate, tributylstannyl cyclopentanecarboxylate and triphenylstannyl cyclopentanecarboxylate were resynthesized according to our reported procedure and theoretically investigated through DFT by applying LANL2DZ as functional with B3LYP basis set (level of theory) to calculate Molecular Electrostatic Potential (MEP) to determine electrophilic center of complexes and Lewis acidity. Owing to the Lewis acid character, the synthesized complexes were then used as catalysts in the transesterification reaction of castor oil. Different reaction parameters were also optimized to obtain maximum biodiesel yield. Synthesized castor oil biodiesel (COB) was characterized and confirmed by employing multitude spectroscopic techniques. The present study evaluated that these complexes can be potential candidates for biodiesel conversion from non-edible and cheap feedstock.

Keywords: Triorganotin(IV) Carboxylates, Theoretical Studies, Castor Oil Biodiesel (COB), Spectroscopic Studies, GCMS

1. INTRODUCTION

Energy demand in the world is continuously increasing as it is one of the important resources for sustainable development. Fossil fuel contributes up to 80 % of total energy and is the main source of mankind's energy demand. According to World Energy Outlook (WEO) 2007, fossil fuels are the major source of producing energy till 2030 and will contribute up to 84 % to meet energy demand [1]. But due to rapid population growth, high demand for energy than total production, environmental issues related to harmful emissions from fossil fuel consumption, reduction of fossil fuels and high rates of fossil fuels world is facing energy crises. Major conventional energy resources petroleum, natural gas and coal are on the verge of extinction and unable to meet future energy needs for a long [2]. So, due to uncertainty about the future supply of fossil fuels, researchers are trying to replace fossil fuels with sustainable, renewable, and trustable energy resources.

Biofuel or biorenewable fuel refers to biogas, bioalcohols [3, 4], vegetable oils [5], biodiesel [6], biohydrogen and pyrolysis oils [7, 8]. Two major important biomass-based liquids are bioethanol and biodiesel which might replace diesel fuel and gasoline in liquid transportation fuels. Biodiesel is methyl- or ethyl ester of fatty acids (FAME) acquired from renewable lipid feedstock through catalytic transesterification reaction in the presence

of organic solvents like methanol or ethanol. Feedstock for biodiesel includes first-generation edible oil plants, non-edible oil crops as second-generation, third-generation algal sources and animal fats [9]. Non-edible oils are preferred as these are not included in human food because of toxic compounds and could be grown in non-cultivated lands [10].

In transesterification reactions, generally, two types of catalysts are employed. In alkali-catalyzed transesterification alkoxide or hydroxides (Bronsted bases) are used but drawbacks of soap formation, as well as wastage of free fatty acid content (10 to 25 %), are associated with this type of catalyst. Alternatively, Bronsted acids are used with the drawback of slow conversion rate and corrosion of the reactor [11]. Recent studies showed that organotin(IV) complexes as catalysts can be a potential candidate in transesterification reactions to produce biodiesel.

These compounds are used in transesterification reactions as catalysts due to their ability to accelerate the reaction between ester and alcohol (by activating the carbonyl carbon of ester for the electrophilic attack of alcohol) because of the Lewis acidity of tin atom and capability of tin(IV) is the expansion of its coordination number. These are mild acids than Bronsted acids so safe in handling and efficient to catalyze a broad range of homogeneous liquid phase reactions. Lewis acidity of tin(IV) increases due to the presence of electron-withdrawing carboxylate ligand and also depends upon the nature of the organic group bonded with tin. Lewis acidity of organotin(IV) carboxylates is higher than their respective chlorides and increases with an increase in the acidic strength of carboxylic acid [12]. The density functional theory (DFT) method is a common method used for theoretical calculations of complexes [13]. Various spectral, structural and Lewis acidity details of the complexes were obtained through DFT calculations [14].

Because of the above-mentioned attractive features of organotin(IV) carboxylates, they were theoretically studied via the DFT method to calculate Molecular Electrostatic Potential (MEP) (to evaluate Lewis character) and tested as catalysts for conversion of castor oil into biodiesel. For the high yield of biodiesel, various reaction conditions were optimized i.e. (time, temperature, oil-methanol ratio and catalyst concentration). The synthesized biodiesel was confirmed by employing FT-IR (ATR), ^{1}HNMR and GC-MS techniques.

2.   MATERIALS AND METHODS

Reagents i.e., $NaHCO_3$, Me_3SnCl, Ph_3SnCl, Bu_3SnCl and cyclopentanecarboxylic acid were attained from Aldrich (USA) and were used as such. Castor oil was purchased commercially from the nearest market of Islamabad, Pakistan. The solvents used in the experiments were purchased from Merck (Germany) and dried accordingly [15]. The melting points were checked in a capillary tube, using Gallen Kamp (UK) apparatus. Bruker Tensor II (ATR) FT-IR spectrophotometer was employed to record the spectra (4000 – 400 cm^{-1}). ^{1}H NMR spectra were recorded on FT-NMR (Burker-300 MHz) spectrometer with DMSO-d6 as solvent [^{1}H (DMSO) = 2.50 ppm]. For GC-MS analysis the GC (GC-6890 N) coupled with MS 5973 MSD fitted with DB-5MS capillary column (30-0.32 mm and 0.25 μm of film thickness) was used.
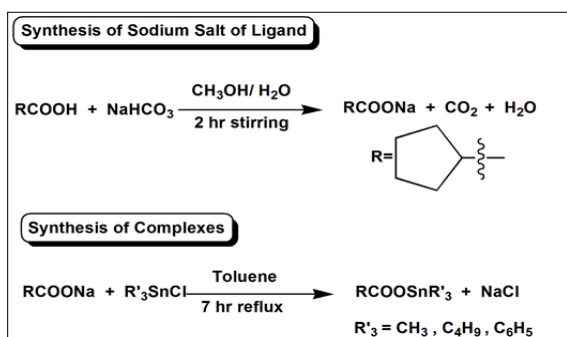
2.1 Synthesis

2.1.1. Synthesis of the Sodium Salt of Ligand

Sodium salt of cyclopentane carboxylate was synthesized according to the reported literature [16] (Scheme 1). Equimolar aqueous solution of $NaHCO_3$ (1.6 g, 20 mmol) was added slowly into the stirring solution of cyclocarboxylic acid-dissolved in methanol (2.16 mL, 20 mmol). The stirring was continued for 2 h at room temperature. Solid product of Sodium Salt of Ligand (NaL) was isolated on a rotary evaporator and then dried. The FT-IR spectroscopy was employed to confirm NaL formation because the OH vibration frequency which is present in the carboxylic acid ligand disappeared. This NaL was then further used as such for complex formation.

2.1.2. Synthesis of Complexes

Trimethylstannyl carboxylate (Me_3SnL), tributylstannyl carboxylate (Bu_3SnL) and triphenylstannyl carboxylate (Ph_3SnL) were resynthesized according to our recently reported method [16] (Scheme 1). Briefly, all the complexes

were synthesized in stoichiometric amounts, sodium salt of the ligand (5 mmol, 0.68 g, 25 mL toluene) in two necks RBF and were refluxed for 7 hours with a solution of trimethyltin chloride in toluene (5 mmol 0.99 g, 25 mL toluene). The reaction mixture was cooled, filtered and transferred to a rotary flask to evaporate toluene under reduced pressure. The crystals of (R_3SnL) were isolated from hexanes: chloroform (3:1). All the complexes were characterized and the data are reported elsewhere [16].

Scheme 1. Synthesis of NaL and its organotin (IV) complexes.

2.2 Computational Studies

Synthesized complexes have been studied theoretically through the density functional theory (DFT) method. The gaussian 09 with LANL2DZ functional with B3LYP as basis set (Lee, Yang and Parr) was used for calculation [17, 18]. Molecular Electrostatic Potential (MEP) was executed to determine Lewis acidity and the electrophilic center of synthesized complexes, respectively.
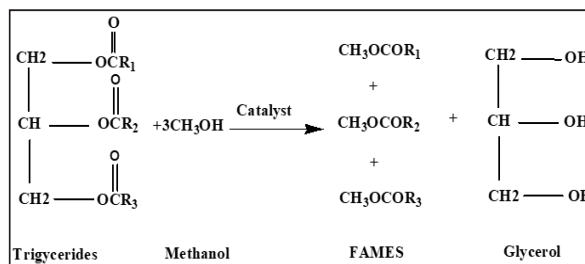
2.3 Transesterification

Owing to Lewis acidity character as determined from the DFT study (NBO analysis) the synthesized organotin(IV) complexes were checked for their catalytic activity towards transesterification of castor oil into biodiesel (Scheme 2) according to reported literature [12]. Before starting the reaction, castor oil was preheated up to 100 °C to remove the moisture. Reactions of castor oil with methanol were carried out following the same protocol (2.1.2.). For maximum yield different parameters of catalytic transesterification reaction i.e., oil to methanol ratio, time, catalyst concentration and

temperature were investigated by performing a series of reactions. Once the reaction is completed, the reaction mixture is kept in a separating funnel overnight for phase separation. The glycerol layer being denser settled down at the bottom and is removed, while the above layer which contains biodiesel was isolated from methanol on a rotary evaporator. The conversion yield was calculated using given equation 1 and through ^{1}H NMR spectroscopy by employing equation 2 [19, 20].

$$\% \ yield = \frac{\text{Grams of methyl ester produced}}{\text{Grams of oil used for reaction}} \times 100 \quad (1)$$

$$\% \ \text{Conversion} = \frac{2A_{Me}}{3A_{CH_2}} \times 100 \quad (2)$$

Where A_{CH2} is integration value for α-methylene peak and A_{Me} is integration value for methoxy peak [21].

Scheme 2. General transesterification reaction.

3. RESULTS AND DISCUSSION

3.1 Molecular Electrostatic Potential (MEP)

MEP of complexes was analyzed by utilizing LANL2DZ functional with B3LYP level of theory. MEP map is used to recognize electrophilic centres in molecules. MEP map results revealed positive charge density on Sn(IV) atoms recognizing them as nucleophilic attack sites (see Figure 1). Red lines surrounding oxygen atoms showed negative charge density on atoms of ligand in complexes. MEP analysis supports that Sn(IV) atoms in complexes have Lewis acid character and hence these complexes become potential candidates for acid catalysts used in transesterification reactions.

3.2 Transesterification

The synthesized organotin(IV) complexes have been used in the conversion of castor oil into
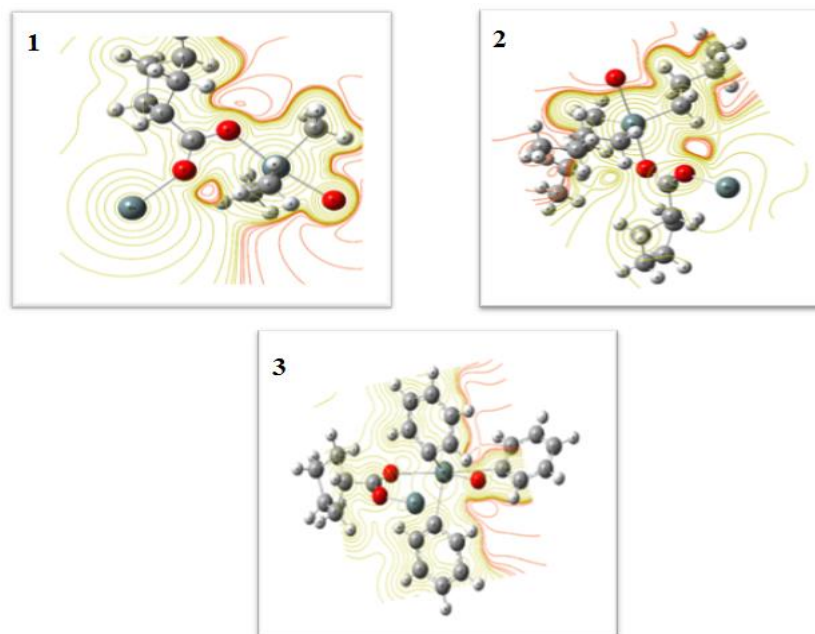
Fig. 1. MEP of complexes 1, 2 and 3.

biodiesel as a catalyst being an eco-friendly and low-cost fuel. To obtain maximum biodiesel yield different parameters have been optimized. These parameters were reaction time, temperature, catalyst concentration and oil-to-methanol molar ratio. Optimization of reaction conditions and comparing their results showed which catalyst is more efficient. The quantification of synthesized biodiesel was checked by using equation 1 (See experimental section).

3.2.1. Optimization parameters for biodiesel synthesis

3.2.1.1 Effect of oil-methanol ratio

For biodiesel synthesis, oil to methanol ratio plays an important role. According to stoichiometry, for every 1 mole of triglyceride, 3 moles of methanol are needed to form 3 ester molecules, so a higher amount of methanol is needed. To obtain optimum oil: methanol, transesterification reaction was carried out by using 1:8, 1:10, 1:12 and 1:14 oil to methanol ratios, keeping catalyst loading 1 % and time 14h at 65°C temperature. It was noticed that initially reaction yield was increased with an increase in methanol ratio which is supported by stoichiometry and a decrease in viscosity favors effective interaction between reactants and catalysts molecules by lowering the mass transfer problem but after 1:12 oil to methanol ratio, the

yield decreases gradually. This decrease in yield at a higher oil-to-methanol ratio is due to the dilution effect. Best yield for complexes 1, 2 and 3 were 95 %, 85 % and 82 % respectively at a 1:12 oil-to-methanol ratio (see Figure 2).
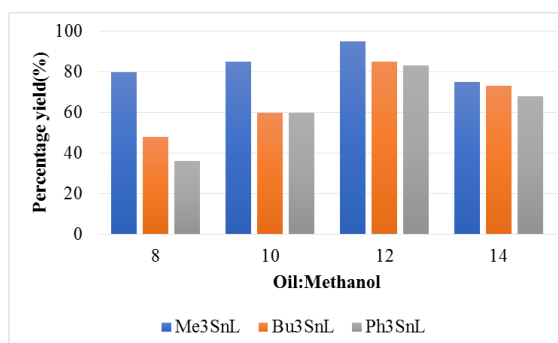

Fig. 2. Effect of oil: methanol on transesterification reaction.

3.2.1.2 Effect of catalyst concentration

Yield in the transesterification reaction was also affected by variations in catalyst concentration. In the present study, four different concentrations (0.5-2 %) of each catalyst have been used at an optimized 1:12 oil to methanol ratio and 14h reaction time. Investigation of obtained results showed the maximum % yield for each complex at 1 % of catalyst concentration (see Figure 3). Initially, biodiesel yield increase with the increase

in catalyst amount indicating an increase in active sites but after a specific concentration decrease in yield occurs which may be possibly due to the coagulation of catalyst in reaction mixture and an increase in viscosity.
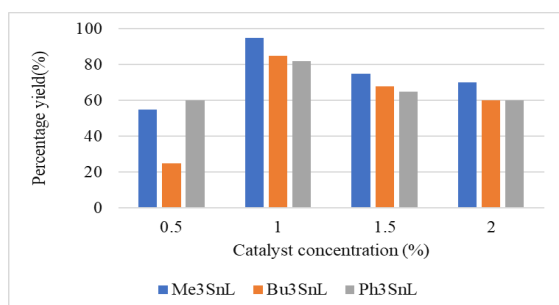

Fig. 3. Effect of catalyst amount on transesterification reaction.

3.2.1.3 Effect of time

In order to understand the effect of time the biodiesel conversion reaction was performed by varying time intervals (1h, 6h, 14h and 24h) by keeping the catalyst and oil to methanol concentration as 1 wt. % and 1:12, respectively. The maximum conversion rate was achieved at 14 hours (see Figure 4). Initially, reaction yield was increased with increasing time but after a certain time, yield decreased. This decrease in yield may be due to blockage of active sites with glycerol molecules which is the byproduct of the reaction.
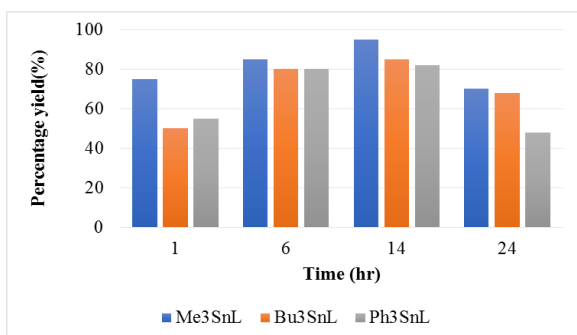

Fig. 4. Effect of time on transesterification reaction.

3.2.1.4 Effect of temperature

The effect of temperature was tested by changing the temperature (45-75 °C) for repeated reactions by maintaining other parameters constant. Initially, biodiesel yield increased with increasing

temperature and a high yield was attained at 65 °C (see figure 5) After that gradual decrease occurs which may be Possibly due to the gasification of methanol.
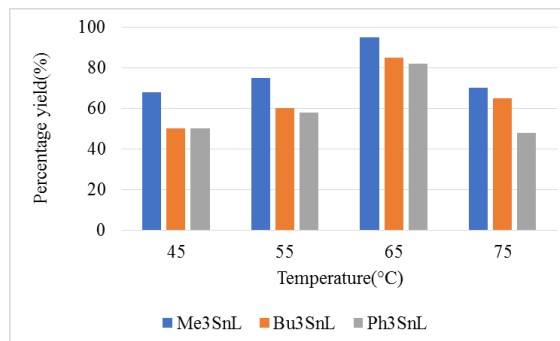

Fig. 5. Effect of temperature on transesterification reaction.

3.3 Spectroscopic Studies of COB

3.3.1. Infrared spectroscopy

FT-IR spectroscopy was employed for synthesized biodiesel to analyze the disappearance and appearance of specific vibrational bands in castor oil and biodiesel spectra. In biodiesel spectrum broad absorption vibration observed in region of 3500-3000 cm^{-1} indicate presence of hydroxyl group in ricinoleic acid [22]. At 1740 cm^{-1} sharp high intensity methoxy peak was observed. Absorption vibration at 3007 cm^{-1} appeared due to sp^2 CH stretch. High intensity absorption vibrations at 2923 cm^{-1} and 2853 cm^{-1} can be ascribed to methyl group. Methyl ester group shows absorption vibration at 1438 cm^{-1}. Other peaks at 1164 cm^{-1}, 1052 cm^{-1} is attributed to O-CH$_3$ stretching vibrations [23]. FT-IR spectrum of COB obtained by using representative catalyst is depicted in figure 6.

3.3.2. ^1H NMR spectroscopy

The ^{1}H NMR spectroscopy was used to characterize castor oil biodiesel and the spectrum is depicted in Figure 7. Due to the presence of FAMEs appearance of two distinct peaks in spectrum confirm the synthesis of biodiesel. One characteristic peak is for methoxy protons as singlets at 3.65 ppm and second peak is for α-methylene (α-CH$_2$) protons as triplets at 2.21 ppm. Other peaks in the spectrum are of terminal methyl protons at 0.87 ppm,
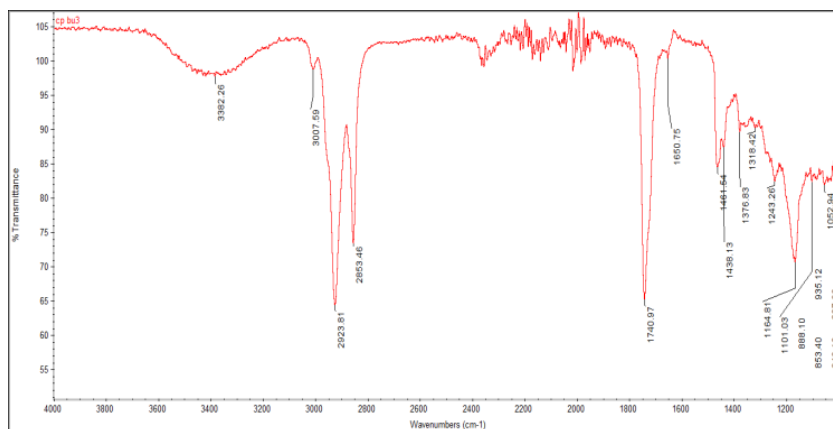
Fig. 6. FT-IR spectrum of COB obtained by using the representative complex as catalyst.
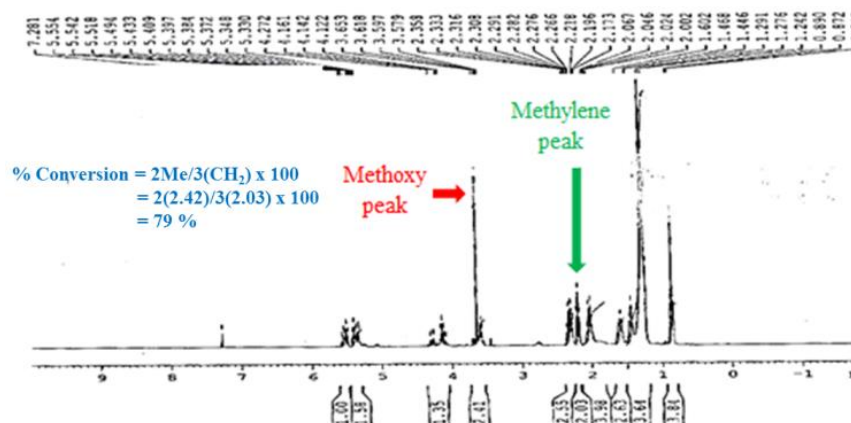

Fig. 7. ¹H NMR spectrum of COB obtained by using representative complex as catalyst.

sharp peak at 1.14 ppm for methylene protons of the carbon chain, β-carbonyl methylene peak at 1.60 ppm, allylic protons peak at 2.0 ppm and olefinic protons signal at 5.3 ppm. Multiplets at 4.31 ppm indicate the presence of glyceridic protons[21]. From ¹H NMR data % is calculated by using equation 2 (See experimental section).

3.3.3. Gas chromatography and mass spectrometry

The chemical composition of castor oil biodiesel and different fragments of FAMEs were confirmed by GC-MS and results are matched with library data software (NO. NIST II). Different fragments have specific retention time. In GC non-polar column was used and thus unsaturated FAMEs eluted in front of saturated ones. Trans-isomers elute after cis-isomer as cis-isomers elute rapidly. A single sharp peak at 14 min in spectra corresponds to Methyl-12-hydroxyoctadeca-9-enoate which is main component of castor oil biodiesel and comprises up to 90 %. GC-MS data depicted that methyl hexadecanoate, methyl 12-hydroxyoctadeca-9-enoate, methyl octadeca-9-enoate and methyloctadeca-9,12-dienoate were the main fatty acid fragments present in COB. The results obtained were in good agreement with the expected composition. The main components of the obtained biodiesel were found to be Ricinoleic acid, linoleic acid and oleic acid methyl esters [24, 25]. GC-MS chromatogram of COB using representative complex as catalyst is depicted in figure 8.
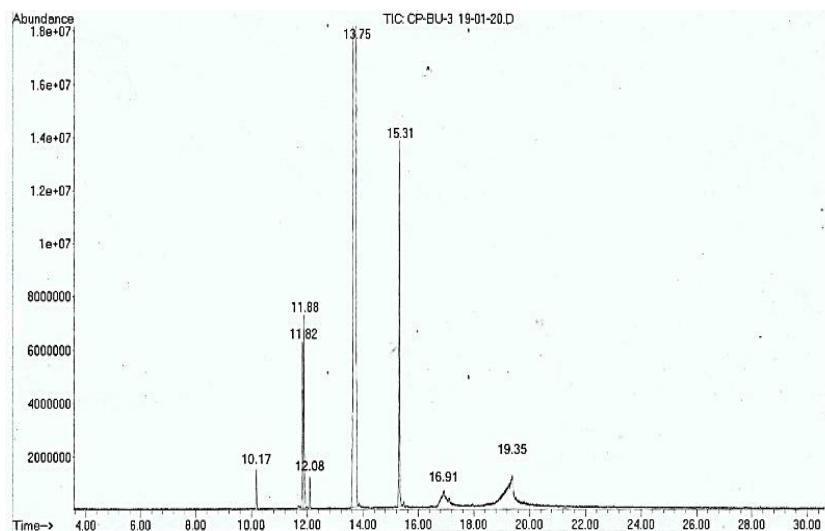
Fig. 8. GC-MS chromatogram of COB using representative complex as catalyst.

4. CONCLUSION

In the present study, three triorganotin(IV) based catalysts were resynthesized and employed for biodiesel synthesis from castor oil through a transesterification process. These catalysts were theoretically studied by MEP map to investigate the Lewis acid character of complexes. These complexes were successfully utilized for the conversion of biodiesel using non-edible castor oil feedstock. Synthesized biodiesel was characterized by FT-IR, ^{1}H NMR and GC-MS. The catalytic application of the assessed compounds was found as follows: Me3SnL > Bu3SnL > Ph3SnL with a maximum conversion efficiency of 95 % under the optimized conditions (oil to methanol ratio 1:12, at 65 °C, for 14 h with catalyst concentrations 1 wt %). From this study it is expected that it will open a new chapter for researchers and biodiesel can be synthesized on a large scale from low-cost castor oil.

5. ACKNOWLEDGEMENTS

6. CONFLICT OF INTEREST

The authers declared that there is no conflict of interest.

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