Catalytic decarboxylation of fatty acids

A Thesis Submitted
In Partial Fulfillment of the Requirements for the
Degree of
Master of Science in Chemistry

By
Parampreet Kaur
(301102007)

Under the supervision of
Dr. Ranjana Prakash
Associate Professor

JULY, 2013
SCHOOL OF CHEMISTRY AND BIOCHEMISTRY
THAPAR UNIVERSITY
PATIALA-147004

Certificate

*This is to certify that the thesis entitled "**Catalytic Decarboxylation of fatty acids** " being submitted in the partial fulfilment of requirements for the award of degree of **Master of Science in Chemistry** submitted in **School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala** is a bonafide work carried under the supervision of **Dr. Ranjana Prakash,** Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and that no part of this project has been submitted for the award of any other degree.*

Parampreet Kaur

(Parampreet Kaur)

This is to certify that above statement made by the student concerned is correct and true to the best of my knowledge.

Supervisor
Dr. Ranjana Prakash
Associate Professor, SCBC,
Thapar University,
Patiala, 147004.

Countersigned by

(Dr.Satnam Singh)
Associate Professor and Head SCBC
Thapar University
Patiala-147004

(Dr.S.K.Mohapatra)
Dean, Academic Affairs
Thapar University
Patiala-147004

ii | P a g e

Declaration

I hereby declared that the work presented in this thesis entitled ***"Catalytic Decarboxylation of fatty acids"*** *submitted in the partial fulfilment of requirements for the award of degree of* ***Master of Science in Chemistry*** *submitted in* ***School of Chemistry and Biochemistry, Thapar University, Patiala*** *is an authentic record of my own work carried out under is a bonafide work carried out under our guidance and supervision and that no part of this project has been submitted for the award of any other degree.*

Date: July, 2013

Place: Patiala

Parampreet Kaur

(Parampreet Kaur)

.....

This is to certify that above statement made by the student concerned is correct and true to the best of my knowledge.

Dr. Ranjana Prakash
Associate Professor, SCBC,
Thapar University,
Patiala, 147004.

iii | P a g e

Acknowledgement

With limitless humility, I would like to praise God the almighty, and the merciful, who bestowed me with all the favourable circumstances to go through this critical junction.

It is my heartfelt pleasure and deepest sense of gratitude to offer my humble and sincere thanks to my esteemed supervisor, ***Dr. Ranjana Prakash, Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala****, for accepting me as a dissertation student and providing precious suggestion, academic excellence, incisive criticism, ineffable faith and an opportunity to access the facilities and resource that were instrumental for the successful completion of my project work. Thank you mam, for believing in me and allowing me to complete my dissertation work.*

I would also like to acknowledge ***Dr. N.Tejo Prakash, Professor, Department of Biotechnology and environment sciences, Thapar University, Patiala*** *for his kind and valuable support.*

I am truly grateful to ***Dr. Satnam Singh, Head of Department, School of Chemistry and Biochemistry, Thapar University, Patiala*** *for his perpetual help and support in the completion of my post-graduate program.*

My deep and sincere gratitude goes to ***Mr. Sumit Jaiswal, Research Scholar*** *who mentored me in every aspect. Sir it was an honor to work with you. Special thanks for your time, patience, understanding, encouragement and above all personal guidance. Your wide knowledge and logical way of thinking has been of great value for me. I also thankful for your valuable guidance in all technical works especially in NMR quantification and to carryout experimental work, last but not least time and unconditional moral support are something which helped me to complete this dissertation work.*

I would like to acknowledge ***Mr.Anirudh Sharma, Research Scholar*** *for his unending support during my project work, you not only taught me the techniques and instrument handling, but also correct me in all my failures during experiments.*

My lab colleagues and friends, you were always so helping and cheerful who always entertained me and was a good company along. Thank you, for making my stay in the laboratory a memorable experience. I can hardly overlook the remarkable cooperation, timely help and moral support extended by my friends.

I would like to express my immense gratitude to my parents, but there are no enough words to thank them for their immense sacrifice, for inspiring me to conceive noble ideas, and teaching me the discipline and the courage to fight for them.

Needless to say errors and omissions are solely mine.

Parampreet Kaur

Parampreet Kaur

iv | P a g e

Summary

Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, is an environmentally attractive alternative to conventional petroleum diesel fuel, generally produced by transesterification with a monohydric alcohol, usually methanol. Biodiesel has many important technical advantages over petrodiesel, such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content, and lower exhaust emissions. However, important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability. To overcome these problems, research is been focused mainly on the production of second generation biodiesel. They are produced through the process of decarboxylation including simple transformation of fatty acids into hydrocarbon based fuel. Second generation biodiesel contains almost all properties of a petro-diesel which simple biodiesel obtained by transesterification is lacking. In the present study, decarboxylation of short to long chain fatty acids were carried out using silver nitrate and lead acetate as a catalyst. Observations of the present study clearly indicate that catalytic efficiency of lead acetate is approximately similar to silver nitrate and shows a good correlation in between catalytic efficiency of both. The use of lead acetate, therefore, is being suggested as an effective alternative for decarboxylation of free fatty acids to produce second generation biodiesel.

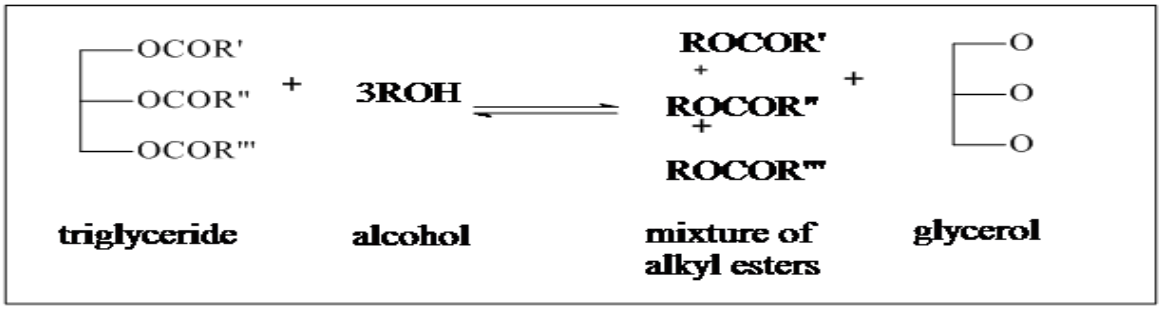
Contents

1. **Introduction** **1-3**
2. **Literature review** **4-10**
3. **Experimental** **11-13**
4. **Result and Discussion** **14-20**
5. **References** **21-27**
6. **Annexure-1** **28-37**

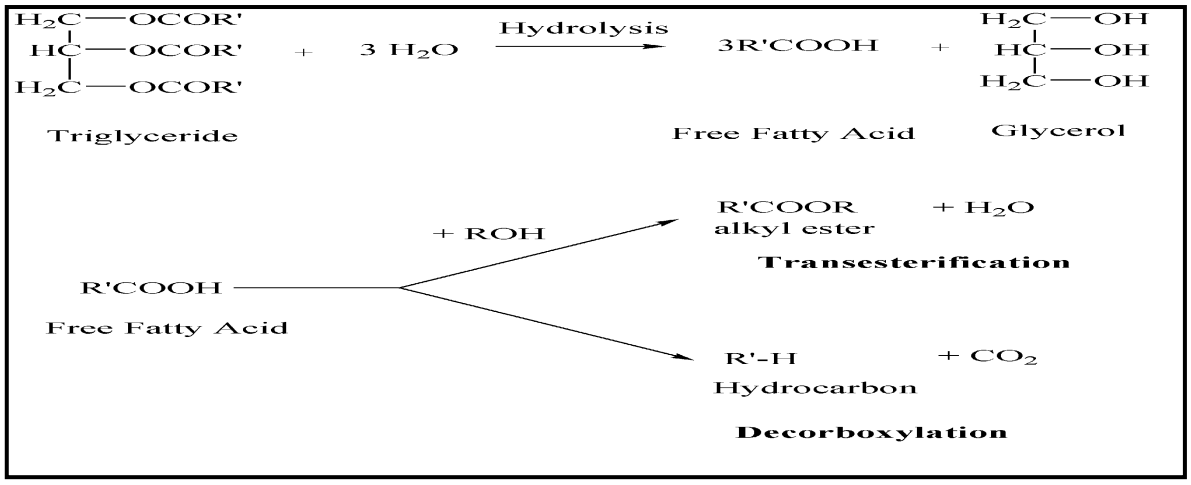
Introduction

Fossil fuels are products formed by natural processes such as anaerobic decomposition of buried dead organisms over long duration. However, due to extensive exploitation post-industrial revolution, the fossil fuels, especially those that are petroleum based, have become scarce and cost-intensive. Due to increasing gap and supply and demand of these fuels such as diesel and petrol, interests in renewable fuels have been encouraged in recent years. One of promising developments in this direction, are the processes that are involved in generation of fuels from vegetable oils.

First generation biofuels, such as fatty acid alkyl esters (FAAEs), are commonly produced by transesterification of triglycerides in vegetable oils with alcohol.



But these FAAEs have many disadvantages such as high viscosity, high cloud point temperature, poor oxidation stability, and low energy density. A better option is to convert fatty acid molecules to hydrocarbons by dislodging their carboxyl group. One of the important reaction to carry out this step is decarboxylation. Decarboxylation is a chemical reaction that removes a carboxyl group and releases carbon dioxide. The term "decarboxylation" chemically involves replacement of the COOH (carboxyl group) with a proton.



The important feature of incorporating decarboxylation step instead of transesterification, results in saturated and unsaturated hydrocarbons that are significantly similar petroleum based fuels.

In majority of industrial processes, reaction of unsaturated fatty acids occurs at the carboxylic acid group, such as amidation, esterification, and chlorination. Nevertheless, many routes to functionalize the double bonds of fatty acids and their derivatives exist, often based on well-known conversions of petrochemical alkenes. Sometimes, the application of petrochemical alkene chemistry with unsaturated fatty acids is hampered, due to the longer chain length or to interactions of the carboxylic acid group with the catalyst, leading to deactivation. Regarding the latter, new chemical opportunities are created when, prior to carbon-carbon double bond conversions, the carboxylic acid functionality of unsaturated fatty acid derivatives is removed. However, the process of decarboxylation involves conditions that require significantly high temperature and pressure conditions leading to cost-intensive and hazardous operation.

A major barrier in the commercialization of hydrocarbon production from fatty acids is its high manufacturing cost, which is due to the higher cost of virgin vegetable

oil. Alternatively, the economics of fatty acid can be significantly improved by the use of the waste vegetable oil. Even though some of this waste cooking oil is used for soap production, a major part of ion is discharged into the environment. The use of waste cooking oil as fatty acid feedstock reduces the cost of hydrocarbon production since the feedstock costs constitutes approximately 70-95% of the overall cost of fatty acid production.

Keeping this in view, the present study attempted to carry out catalytic decarboxylation of commercial and biologically generated fatty acids at normal temperature and pressure.

Literature Review

From the past years, research is been focused mainly on the production of second generation biodiesel. Second generation biodiesel is also called as Advanced biofuels. They are formed by the process of decarboxylation including simple transformation of biodiesel into hydrocarbon base fuel. The product formed contains less carbon as compared to the reactants. Second generation biodiesel contains almost all properties of a diesel which simple biodiesel obtained by transesterification is lacking. Deoxygenation of vegetable oils or animal fats yields hydrocarbons similar to those found in regular diesel fuel. Such biofuels have higher energy densities and higher storage stabilities than first generation biodiesel because of the absence of oxygen containing functional groups and are fully compatible with existing vehicles and fuel infrastructures. Several technologies are known to produce liquid fuels from biomass, summarized in recent reviews (Regalbuto 2011).

Biodiesel is currently the most commonly used biofuel in Europe and is produced by transesterification of triglycerides (main constituent of vegetable oils and animal fats) with methanol using a homogeneous base catalyst (Bondioli 2004). Although the resulting fatty acid methyl esters (typical first generation biodiesel) have desirable fuel qualities such as good cetane number and lubricity, there are many technical issues associated with widespread use, like poor storage stability, lower heat content and engine compatibility issues compared to regular diesel fuels due to the high cloud and pour point (Geyer et al. 1984). In the literature, pyrolysis (Lima et al. 2004, Adebanjo et al. 2005, Maher et al. 2007, Higman et al. 1973), hydrodeoxygenation (Choudhary et al. 2011,

Sotelo-Boyaa´s et al, 2011, Stumborg et al. 1996, Matsoukas et al. 2009) and deoxygenation (Fisk et al. 2009) are reported for the production of second generation biodiesel.

Hydrodeoxygenation (HDO) includes mainly three reaction mechanisms. They are decarbonylation (DCN), decarboxylation (DCX), and reductive deoxygenation without C−C cleavage (RDO). The process of reductive deoxygenation (RDO) is quite different from the other two reaction mechanisms. The main difference is that in case of RDO, all oxygen atoms in the organic acid are removed in the form of water requiring a substantial amount of hydrogen, while in the DCN and DCX mechanism most of the oxygen is removed in the form of CO_2 and CO (Lu et al. 2012). There is a need of HDO catalysts favouring the DCN and DCX pathway over the RDO pathway (Centi et al. 2007). In this case, Pd/SiO_2 catalysts are mainly selected for the deoxygenation of carboxylic acids (Maier et al. 1982). Various research groups conducted an extensive investigation of the liquid phase HDO of various long chain fatty acids such as lauric acid (Maki-Arvela et al. 2008), palmitic acid (Simakova et al.2008, Lestari et al. 2009) and stearic acid (Lestari et al. 2009, Simakova et al. 2009) on Pd/C catalyst and it is suggested that decarboxylation is the most dominant as compared to that of decarbonylation (DCN) or reductive deoxygenation (RDO). In general, Pd/C is best among Pd, Pt, Ni, Rh, Ir, Ru, and Os (Snare et al. 2006).

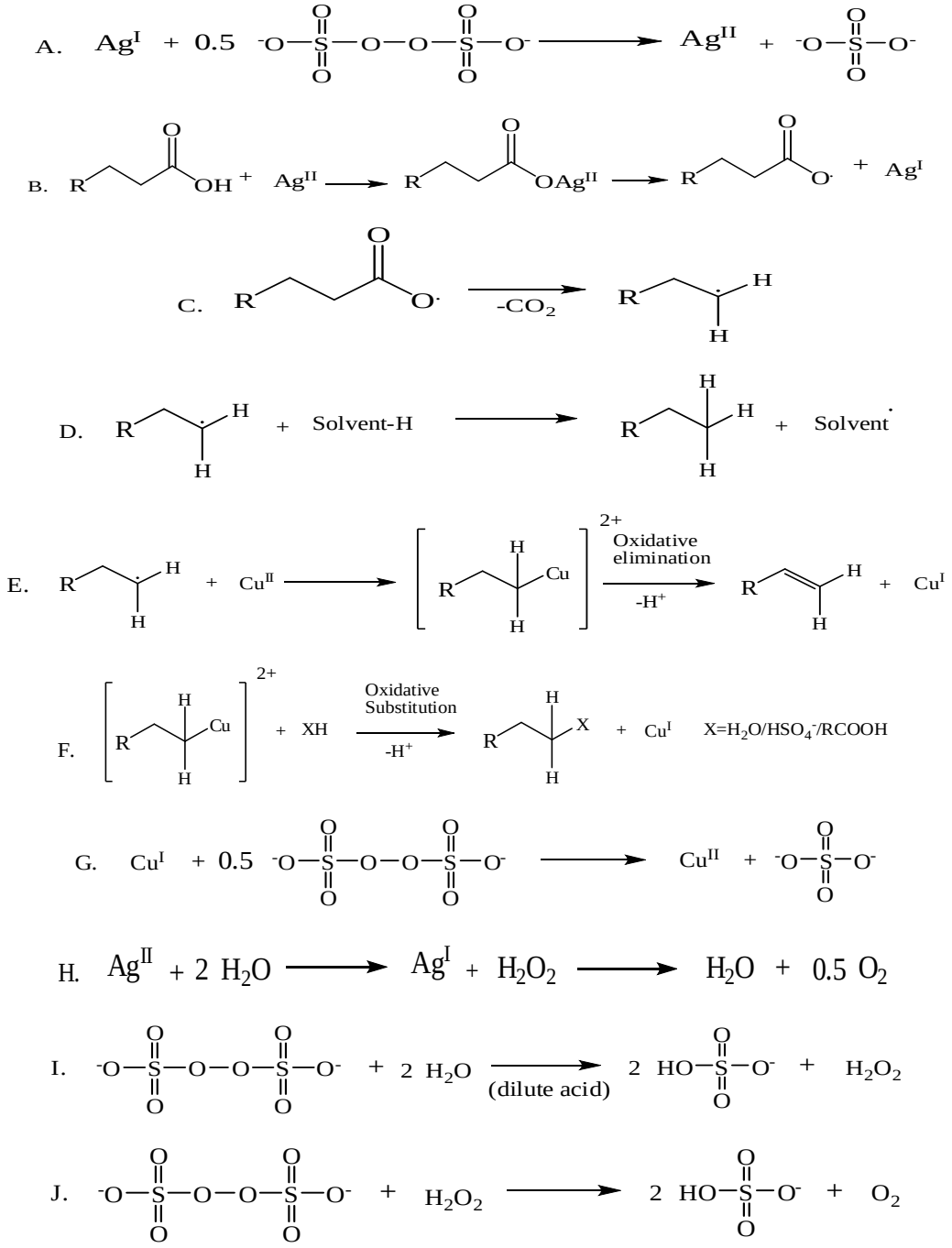
Heterogeneous catalysts have also been developed in the recent years for the biodiesel preparation, but there are many limitation such as requirement of higher temperature and pressure (temperature around 200–250° C) (Huber et al. 2006). In addition to this, product cost increases by the post treatment of glycerol by-product.

Homogeneously palladium-catalyzed decarboxylation reactions of active allyl esters have been reported in the literature. Using aliphatic acid methyl esters and ethyl esters as model compounds, the catalytic performance of $Pd/BaSO_4$ was examined. Several catalysts which are palladium-based were also examined including $Pd/SrSO_4$, $Pd/BaCO_3$, $Pd/CaCO_3$, Pd/C and Pd/MWCNTs (Pd metal on multi-walled carbon nanotubes).

Mainly literature describes the use of elevated hydrogen pressures and temperatures (3–10 MPa, 550–620 K) for the production of second generation biodiesel from vegetable oils (Kalnes et al. 2007, Myllyoja et al. 2007). Especially the need for (non-renewable) hydrogen remains a challenge to overcome. Furthermore, the use of hydrogen results in the reduction of double bond functionalities present in unsaturated oils or fatty acids which reduces their potential application in high value chemical production. A further drawback of the current technology is the concomitant hydrodeoxygenation of glycerol to propane, which consumes valuable hydrogen and hinders potential commercial value of the glycerol. Saturated fatty acid like Stearic acid is a commonly used model compound in fatty acid deoxygenation reactions for more realistic feedstocks like rape seed and palm oil fatty acids. Many deoxygenation studies, concerning stearic acid or other closely related model compounds, have been published in recent years using various catalysts under inert (Snare et al. 2006, Simakova et al. 2010), hydrogen (Do et al. 2009, Han et al. 2010) or hydrothermal conditions (Matsubara et al. 2004). The deoxygenation of such free fatty acids can proceed via decarboxylation, decarbonylation–dehydration or hydrogenation yielding heptadecane, heptadecene or octadecane, depending on which reaction takes place.

Palladium catalysts are often used in deoxygenation reactions since (Snare et al. 2006) performed a catalyst screening study, which reported Pd/C as the most active and selective catalyst (Snare et al. 2006). $Pd/\gamma\text{-}Al_2O_3$ and $Pt/\ \gamma\text{-}Al_2O_3$ were the most effective of the metal oxide supported catalysts, giving only small amounts of ketonized or heavy by-products (Snare et al. 2006). Mechanistic proposals for the catalytic deoxygenation of aliphatic esters under a hydrogen atmosphere over heterogeneous palladium catalysts were reported by (Han et al 2010). Here alkyl–oxygen and acyl–oxygen cleavage were proposed for decarboxylation and decarbonylation mechanisms (Han et al. 2010). Stearic anhydride is proposed as reactive intermediate in the hydrogen free decarbonylation and ketonization of stearic acid over Pd/Al_2O_3 at 523 K. Product selectivity of stearic acid deoxygenation at 523 K is strongly dependent on the feed concentration with selective decarboxylation at the low end and increasing decarbonylation and ketonization activity at higher feed concentrations (Stefan et al. 2012).

(Anderson and Kochi et al. 1970 (a, b)) reported the use of silver (II) in the decarboxylation of C4/C5 carboxylic acids to form alkanes. Catalytic silver (I) was oxidized in situ to silver (II) by stoichiometric amounts of readily available peroxydisulfate. When catalytic copper (II) was added, 1-alkenes and alcohols were formed. However, a vast excess of carboxylic acid was used, limiting the synthetic potential (Fristad et al. 1983). When the reaction takes place in the additional presence of copper (II) similar to saturated carboxylic acids, 1-alkenes were the major decarboxylation product. But when the reaction takes place in the absence of copper (II) alkanes were predominantly formed. This is a free radical based decarboxylation and mechanisms proposed by (Klis et al. 2011) are as follows:



On the basis of versatile oxidizing agents known in organic chemistry, lead (IV) acetate has been also been extensively used. It has the capability to react with variety of common functional groups. Here also the main purpose is the decarboxylation process according to the experimental conditions e.g., solvent, structure of substrates, and

presence of additives. This catalyst is applicable for the conversion of carboxylic acids into variety of compounds including oxidative process. The main purpose here is the usefulness of this reaction in organic synthesis. From many years the process of decarboxylation of alpha-hydroxy and alpha-amino acids by lead (IV) acetate has been known. The exhaustive products study of lead tetra acetate in acetic acid is reported. The reduction of lead tetra acetate was accelerated by sodium acetate but carbon dioxide is not liberated by lead (IV) acetate. Thermal decomposition of various organic acids was also examined. Till date, studies related to modifications, the mechanisms and synthetic utility of these reactions (Sheldon et al. 2011) have been reported on lead (IV) acetate. In many cases, lead (IV) acetate is used for the production of second generation biodiesel by the process of decarboxylation as lead (IV) acetate is well known oxidizing agent (Wilberg 1965). In the presence of catalytic amounts of Cu (II) the conversion of carboxylic acids to terminal olefins having one less carbon atom is found to be very effective using lead (IV) acetate. In this reaction method, the main advantage is that the temperature conditions are manageable i.e. 80° C and the side products are also very less. Drying oil derived fatty acids contain very reactive internal unsaturation. The reaction containing low temperature makes it ideal for decarboxylation. By using pyridine and lithium acetate as a catalyst, 17 carbon terminal polyolefins are formed from unsaturated fatty acids with lead (IV) acetate (Carlblom et al. 1973). The rapid decarboxylation under these conditions can be instantaneously interrupted with oxygen, and remains completely inhibited for prolonged (and indefinite) period of time and not until the oxygen is removed (Kochi 1965).

Although extensive studies have been carried out on decarboxylation of fatty acids using variety of catalysts, most of the reports are focused on excuting reactions in high temperature and pressure. The present study, therefore, aimed at identifying a suitable catalyst and developing a protocol for decarboxylation of fatty acids at normal temperature and pressure. A comparison has also been drawn with few reported methods in literature that have been attempted at normal temperature and pressure.

Experimental

Materials

Hexanoic acid, heptanoic acid, octanoic acid, decanoic acid, palmitic acid, stearic acid, oleic acid, silver nitrate, lead (II) acetate, acetonitrile, sodium persulphate, sodium hydrogen bicarbonate, hexane and diethyl ether were purchased from S.D fine chemicals (Mumbai, India). All the reagents were analytical grade and used without any further purification. Three different free fatty acids (FFA) were generated from waste edible oils (cotton seed, rice bran and ground nut oil) through fungus mediated hydrolysis.

Free fatty acid generation from waste cooking oil

Different edible waste cooking oils (cotton seed, rice bran and ground nut oil) were collected from the different sources viz., student dormitory and cafeteria. All the samples were collected after extensive frying of 2-5 h. Fungal strain, *Aspergillus* sp. (MTCC 5436) isolated previously from clarified butter was used to carry out hydrolysis of waste edible oil. Complete hydrolysis of oil into FFA were obtained using Bushnell-Haas broth (BHB) containing $MgSO_4$ (0.2 g/l), $CaCl_2$ (0.02 g/l), KH_2PO_4 (1.0 g/l), K_2HPO_4 (1.0 g/l) and $FeCl_3$ (0.05 g/l) and supplemented with mycological peptone (0.5% w/v), $(NH_4)_2HPO_4$ (0.5% w/v) as nitrogen sources and different waste edible oils as a carbon source. Culture was inoculated in growth medium incubated at 30° C at 120 rpm for 120 h to carry out hydrolytic reaction. Thin layer chromatography (TLC) was used to monitor the hydrolysis of oil into FFA. After complete hydrolysis, FFAs were isolated from reaction mixture using hexane as an extracting solvent, dried over anhydrous

sodium sulphate and hexane removed by rotatory evaporator. Separated FFAs were used for further decarboxylation.

Oxidative decarboxylation of different fatty acids by silver nitrate and lead acetate

Oxidative decarboxylations of fatty acids were carried out by the method given by (Klis et al. 2011). Reactions were carried out in a 250 ml round-bottom three-necked flask, placed on a magnetic stirrer and connected to reflux condenser and dropping funnel. The reaction mixture was refluxed at 78°C. All the reactants were used in 1:1 molar ratio, for example oleic acid (2.0 g, 7.08 mmol), silver nitrate (1.2 g, 7.08 mmol) or lead (II) acetate (4.0 g, 7.08 mmol), and 50 ml water or 90 ml acetonitrile. Subsequently, an aqueous solution of sodium persulfate (3.71 g / 15.6 mmol in 40 ml of water) was added drop-wise within 10 min. When addition was complete, the reaction mixture was stirred at reflux temperature for an additional 10 min and rapidly cooled to room temperature using an ice bath. The reaction mixture was extracted thrice with 10 ml diethyl ether and the combined organic layers were washed with a saturated $NaHCO_3$ solution. A little brine was added to prevent the formation of an emulsion. The organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure at 40° C with a rotary evaporator to give the crude product and percentage decarboxylation were quantified using ^1H NMR (400 MHz; Jeol JNM-ECS 400). $CDCl_3$ (deuterated chloroform) was used as solvent and tetra methyl silane as internal standard. ^1H NMR spectra were recorded with pulse duration of 2.18 sec with a relaxation delay of 4 sec and 16 scans.

Proton nuclear magnetic resonance (^{1}H NMR) based quantification of decarboxylation reaction

^{1}H NMR spectroscopy was used for quantitative determination of hydrocarbon generated through oxidative decarboxylation reaction of different fatty acids. In present work, percent conversions of fatty acids were derived by a new formula that is being proposed here. This formula is based on change in integration value of NMR spectrum of α-CH_2 peak (2.3 ppm) of fatty acid and terminal –CH_3 (0.89 ppm) peak in product.

$$\% \text{ Conversion} = 100 - [(I_{\alpha\text{-}CH2} \times 3) / (I_{t\text{-}CH3} \times 2)] \times 100$$

$I_{\alpha\text{-}CH2}$ - Integration of α-acyl methylenic hydrogen at 2.3 ppm

$I_{t\text{-}CH3}$ - Integration of terminal –CH_3 at 0.89 ppm

Results and discussion

A set of decarboxylation experiments with short to long chain fatty acids (including free fatty acids generated from waste edible oils) were performed using silver nitrate and lead (II) acetate as a catalyst. **Table 1** presents the ^{1}H NMR based observations on decarboxylation which show that the extent of decarboxylation increased with increase in chain length of fatty acids. **Annexure 1** presents the ^{1}H NMR spectra of products derived through decarboxylation of fatty acids, as catalyzed by silver nitrate and lead (II) acetate.

Table 1. Percentage conversion of different fatty acids in to respective hydrocarbons using silver nitrate and lead (II) acetate as a catalyst, along with the decarboxylation of pure vegetable oils

S.No	Fatty Acid	Silver nitrate			Lead (II) acetate		
		$I_{\alpha\text{-}CH2}$	$I_{t\text{-}CH3}$	% Conversion	$I_{\alpha\text{-}CH2}$	$I_{t\text{-}CH3}$	% Conversion
Fatty acids							
1	Hexanoic acid	2.0	3.19	5.95	2.0	3.64	17.58
2	Heptanoic acid	2.0	4.38	31.50	2.0	4.29	30.06
3	Octanoic acid	2.0	6.08	50.65	2.0	8.1	62.96
4	Decanoic acid	2.0	7.01	57.20	2.0	6.38	52.97
5	Oleic acid	2.11	9.25	65.78	2.0	9.55	68.58
6	Palmitic acid	2.0	13.03	76.97	2.0	7.17	58.15
7	Stearic acid	2.0	11.3	73.45	2.0	6.74	55.48
Fatty acids derived from used vegetable oils							
8	Cottonseed	2.15	9.46	65.90	2.0	10.5	71.42
9	Rice bran	2.16	8.59	62.28	2.3	11.86	70.9
10	Ground nut	2.12	12.17	73.87	2.65	16.35	75.68

Catalyst like silver nitrate and lead (IV) acetate were previously reported for oxidative decarboxylation of different aliphatic fatty acids (Klis et al. 2011, Kochi 1965, Carlblom et al. 1973) but to the best of our knowledge, there is no report on the use of lead (II) acetate as catalyst for oxidative decarboxylation. The decomposition of lead (II) acetate in the presence of fatty acid is presumed to follow a similar pathway as that described for silver nitrate (Klis et al. 2011) and the observations of the present study as shown in Table 1 clearly indicates that catalytic efficiency of lead (II) acetate is approximately similar to silver nitrate further confirming the hypothesis. Klis et al. (2011) used silver nitrate and silver nitrate with copper (II) sulphate pentahydrate for decarboxylation of different fatty acids like oleic acid, linoleic, elaidic, erucic, linolenic, ricinoleic, palmitic and stearic acid and % conversion were ranges from 80-99 %, when determined by GC using hexadecane as internal standard. Use of lead (II) acetate might be an alternative and cost effective catalyst for decarboxylation of free fatty acids to produced second generation biodiesel. In addition, the study also indicates that with the increase in carbon number of the fatty acids, the reaction and and hydrogen consumption increased with simultaneous decrease in carbondioxide selectivity and initial decarboxylation rate. The influence of alkyl chain length on decarboxylation was investigated for a homologous series of C_{10}–C_{18} fatty acids using the Pd/C catalyst (Ford et al. 2012).

A number of analytical techniques have been employed to examine fuel components and for specific compound classes within the fuel (Shonetta et al. 2006). Analysis of fuel and its components has been attempted using gas chromatography, using mass spectrometry, flame ionization, electron capture and photoionization detection. Gas

chromatography is the predominant mode for the determination of fuel mixture. Quantitative determination of the product obtained from decarboxylation of fatty acids were analyzed by GC with hexadecane as internal standard and ^{1}H and ^{13}C NMR were used for qualitative determination of product formed (Klis et al. 2011), whereas limited reports are available on NMR based quantification of hydrocarbons formed during decarboxylation process Therefore, present work was mainly focused on development and validation of the formula used for quantification of hydrocarbons.

NMR spectroscopy has become one of the most powerful tool to look into and identify the structure of chemical compound and dynamics of any ongoing chemical reaction (Silverstein et al. 2005), since very less amount of samples are required to obtained a quantitative spectrum with significant information related to samples and reaction mixture. Biodiesel esters quantification by ^{1}H NMR is a simple and faster technique in comparison with time consuming gas chromatography and HPLC (Knothe 2006). Free glycerin and acid number can also be determined by ^{1}H NMR and present a nice correlation with official methods data (ASTM D6584 and ASTM D664). The application of ^{1}H NMR spectroscopy has recently been used to monitor the kinetics and product distributions in transesterification reactions (alcoholysis) between vegetable oils and alcohols (Suppes et al.2001, Knothe 2000, Gelbard et al.1995). The use of ^{1}H NMR is convenient and fast when monitoring a reaction, because a small aliquot can be extracted from the batch reaction at any given time and the ^{1}H NMR spectrum analysis provides quantitative information pertaining to the chemical species present in the reaction (Morgenstern et al. 2006). First time ^{1}H NMR analysis was used for quantification of methyl esters by simple equations (Knothe 2000, Gelbard et al.1995)

and these equations includes change integration values of proton signals in both reactants and products. Silva (2005) proposed a revised formula for NMR based quantification of ethyl ester and this formula was further modified by Ghesti et al. (2007). Further, Knothe (2000) correlated near-infrared (NIR) spectroscopy and two ^{1}H NMR equations with good agreement. Neto and co-workers (2004) correlated their ^{1}H NMR analytical curves with viscosity measurements, obtaining a linear correlation coefficient of 0.99. Similarly, our research group proposed a formula which can be applied for the quantification of alkyl esters having primary alcohols other than methanol and ethanol as acyl acceptors (Sharma et al. 2013).

However, most of the derivations were focused on quantification of alkyl esters synthesized using various catalytic routes. To the best of our knowledge, there is no NMR based derivation for quantification of hydrocarbons, especially alkanes, derived through decarboxylation reaction. Keeping this in view, a new derivation is being proposed through this study, wherein ^{1}H NMR data has been used for quantification of aliphatic hydrocarbons produced by decarboxylation of fatty acids. This formula, as explained in methodology earlier, is based on change in integration value of NMR spectrum of α-CH_2 peak (2.3 ppm) of fatty acid and terminal –CH_3 (0.89 ppm) peak in product.

$$\% \text{ Conversion} = 100 - [(I_{\alpha\text{-}CH2} \times 3) / (I_{t\text{-}CH3} \times 2)] \times 100$$

$I_{\alpha\text{-}CH2}$ - Integration of α-acyl methylenic hydrogen at 2.3 ppm

$I_{t\text{-}CH3}$ - Integration of terminal –CH_3 at 0.89 ppm

In proposed formula integration value of NMR spectrum of α-CH_2 peak (2.3ppm) and terminal –CH_3 peaks (0.89 ppm) has been taken in consideration. Decarboxylation

reaction results in dislodging of –COOH group from fatty acid, and subsequent formation of CO_2 and a final product corresponding to a hydrocarbon. With increase in decarboxylation, the number of terminal $–CH_3$ groups increase and extent of decarboxylation can be directly determined by increased signal of terminal $-CH_3$ in ^1H NMR. For example, in ^1H NMR spectrum of pure oleic acid, integration values α-CH_2 peak is equivalent to two hydrogen atoms, whereas, terminal $–CH_3$ group is equivalent to three hydrogen atoms (Fig. A) whereas after decarboxylation integration value of terminal $–CH_3$ increases (Fig. B).

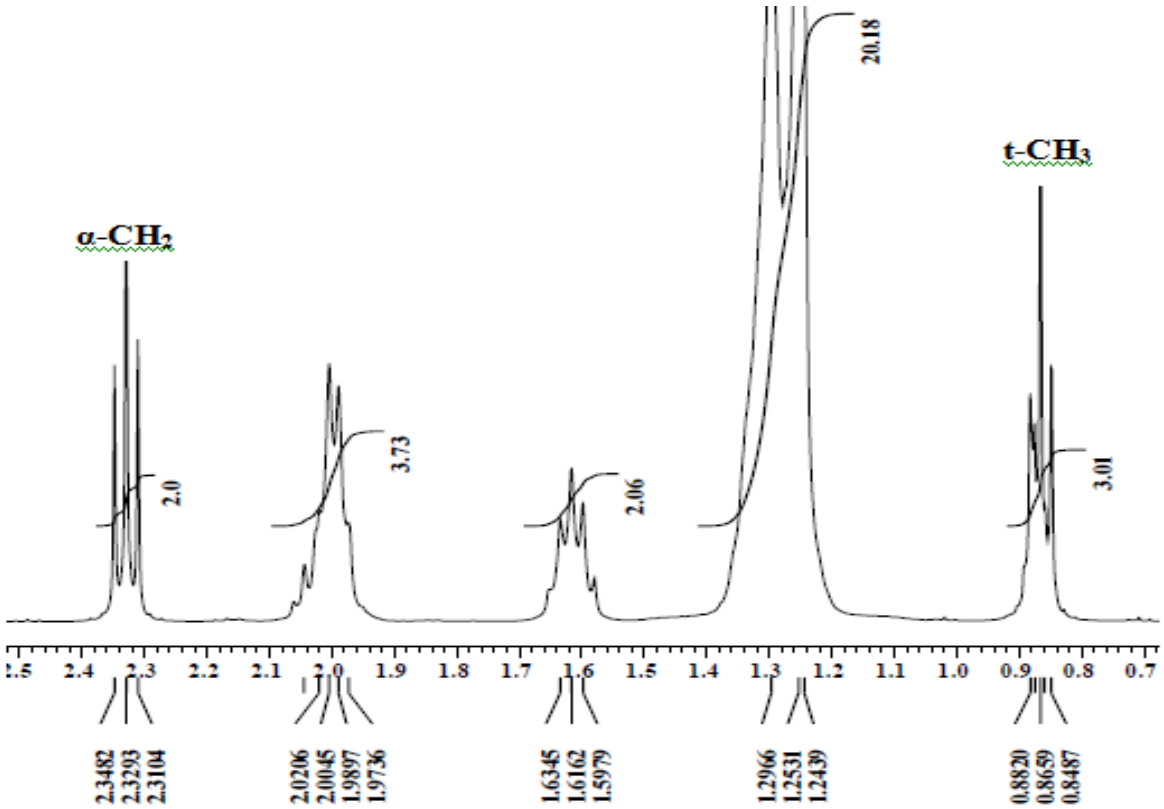


Figure A. 1H NMR of pure oleic acid

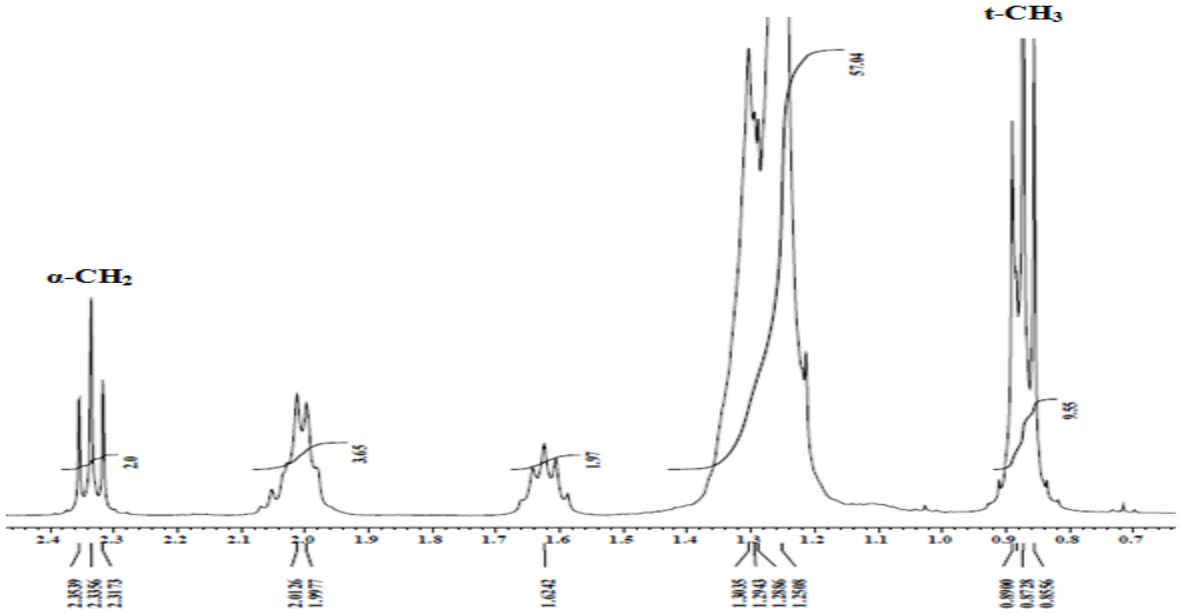


Figure B. ^{1}H NMR of the decarboxylation products of oleic acid

In the case of pure oleic acid, integration values of α-CH_2 ($I_{\alpha\text{-}CH2}$) and terminal-CH_3 ($I_{t\text{-}CH3}$) are 2.0 and 3.0, whereas in decarboxylation, product integration values are 2.0 and 9.55 respectively. According to the proposed formula, conversion oleic acid to its corresponding product, through decarboxylation reaction is from 0% and 68.58%. Similarly, Table 1 presents the percent conversion of other fatty acids into their respective hydrocarbons, which has been determined by the above derivation by taking α-CH_2 and terminal-CH_3 into consideration.

Traditionally, biodiesel is synthesized through transesterificaion of oils and fats with methanol. Although biodiesel has many advantages in comparison with petrol diesel, it suffers from drawbacks such as poor storage stability due to the presence of oxygen. Therefore, decarboxylation is one of the approaches attempted for production of hydrocarbon fuel from the oxygen-containing compounds. Biodiesel produced via decarboxylation is usually called the second generation of biodiesel or "Green" diesel. "Green" diesel in turn has numerous advantages such as high cetane number, higher

energy content, excellent combustion quality, good low-temperature properties (viscosity, freeze point, pour point, and cloud point), and superior thermal stability, storage stability, and materials compatibility in comparison with both petrol diesel and biodiesel (Li et al. 2010). Fatty acids and their derivatives (methyl or ethyl esters) as well as triglycerides can be used as the raw material in the decarboxylation process. A major barrier in the commercialization of second generation biodiesel production from vegetable oil is its high manufacturing cost, which is due to the higher cost of virgin vegetable oil. The cost of vegetable oil has a crucial role in the economics of the biodiesel. The distribution of the cost of biodiesel production indicated that oil feedstock incurs the major cost of biodiesel production accounting over 70% of the total cost (Nelson et al. 1996). Alternatively, the economics of second generation biofuel can be significantly improved by the use of the waste vegetable oil as biodiesel feedstock. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. The use of waste cooking oil as biofuel feedstock reduces the cost of hydrocarbon production since the feedstock costs constitutes approximately 70-95% of the overall cost.

To the best of our knowledge no reports are available on aliphatic hydrocarbon production using free fatty acids as a feedstock generated from waste edible oils, specially using lead (II) acetate as a catalyst for decarboxylation. Therefore, in conclusion, the present study (a) demonstrates the use of cost-effective catalyst viz., lead (II) acetate for catalyzing decarboxylation of fatty acids or fatty acids derived from waste edible oils to their corresponding hydrocarbons; and (b) proposes a derivation for quantification of hydrocarbons based on ^{1}H NMR data.

References

Adebanjo, A. O., Dalai, A. K. and Bakhshi, N. N. (2005). Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat. *Energy Fuels*, **19** (4):735–1741.

Anderson, J. M., Kochi, J. K. (1970) (a). Silver (I)-catalyzed oxidative decarboxylation of acids by peroxydisulfate. The role of silver (II). *J. Am. Chem. Soc*, **92**:651–1659.

Anderson, J.M., Kochi, J. K. (1970) (b).Silver (II) complexes in oxidative decarboxylation of acids. *J. Org. Chem*, **35**:986–989.

Behr, A., Gomes, J. P. (2010). The refinement of renewable resources: New important derivatives of fatty acids and glycerol. *Eur. J. Lipid Sci. Technol*, **112**: 31–50.

Bondioli, P. (2004). The preparation of fatty acid esters by means of catalytic reactions. *Top. Catal*, **27**:77-82.

Carlblom, L.H., Khoe, T.H., Rheineck, A. E. (1973). Olefins from drying Oil Fatty Acids by Catalytic Oxidative Decarboxylation. *75*, **6**:388-392.

Centi, G., Santen, R.A.V. (2007) Catalysis for Renewables: From Feedstock to Energy Production. *Wiley-VCH: Weinheim*.

Choudhary, T. V. and Phillips, C. B. (2011). Renewable fuels via catalytic hydrodeoxygenation. *Appl. Catal. A*, **397**:1–12.

Do, P., Chiappero, M., Lobban, L. and Resasco, D. (2009). Catalytic deoxygenation of methyl-octanoate and methyl-stearate on Pt/Al2O3. *Catal. Lett*, **130**:9–18.

Fisk, C. A., Morgan, T., Y.Y. Ji, Crocker, M., Crofcheck, C. and Lewis, S. A. (2009). Bio-oil upgrading over platinum catalysts using in-situ general hydrogen. *Appl. Catal. A*, **358**(2):150–156.

Fristad, W. E., Fry, M. A., Klang, J. A. (1983). Persulfate/silver ion decarboxylation of carboxylic acids. Preparation of alkanes, alkenes, and alcohols. *J. Org. Chem*, **48**:3575–3577.

Ford, J. P., Immer, J. G., Lamb, H. H. (2012). Palladium Catalysts for Fatty Acid Deoxygenation: Influence of the Support and Fatty Acid Chain Length on Decarboxylation Kinetics. *Top Catal*, **55**:175–184.

Fu, J., Lu, X and Savage, P. E. (2010). Catalytic hydrothermal deoxygenation of palmitic acid. *Energy Environ. Sci*, **3**:311–317.

Fu, J., Lu, X and Savage, P.E. (2011). Hydrothermal decarboxylation and hydrogenation of fatty acids over Pt/C. *ChemSusChem,* **4**:481-486.

Gelbard, G., Bres, O., Vargas, R. M., Vielfavre, F., Schuchardt, U. F. (1995). ^{1}H Nuclear Magnetic Resonance Determination of the Yield of the Transesterification of Rapeseed Oil with Methanol. *J. Am. Oil Chem. Soc*, **72**: 1239-1241.

Geyer, S. M., Jacobus, M. J. and Lestz, S. S. (1984). Comparison of Diesel Engine Performance and Emissions from Neat and Transesterified Vegetable Oils. *Transactions of the ASAE*, **27**:375–381.

Ghesti, G. F., Macedo, J. L., Resck, I. S., Dias, J. A., Dias, S. C. L. (2007). FT-Raman Spectroscopy Quantification of Biodiesel in a Progressive Soybean Oil Transesterification Reaction and Its Correlation with 1H NMR Spectroscopy Methods. *Energy Fuels*, **21**: 2475–2480.

Han, J., Sun, H., Ding, Y., Lou, H. and Zheng, X. (2010). Palladium-catalyzed decarboxylation of higher aliphatic esters: Towards a new protocol to the second generation biodiesel production. *Green Chem*, **12**:463–467.

Higman, E. B., Schmeltz, I., Higman, H. C. and Chortyk, O. T. (1973). Studies on the thermal degradation of naturally occurring materials II. Products from the pyrolysis of triglycerides at 400°C. *J. Agric. Food Chem,* **21**:202–204.

Huber, G.W., Iborra, S. and Corma, A. (2006). Synthesis of transportation fuels from Biomass: Chemistry, Catalysts and Engineering. *Chem. Rev*, **106**:4044-4098.

Immer, J.G., Kelly, M.J and Lamb, H.H. (2010). Catalytic reaction pathways in liquid-phase deoxygenation of C18 free fatty acids. *App catal A,* **375**:134-139.

Kalnes, T., Markery, T. and Shonnardz, D. R. (2007). Green diesel: A second generation biofuel. *Int. J. Chem. React. Eng*, **5**:1–9.

Klis F. van der., Hoorn, M. van den., Blaauw R., Haveren J. Van., Es, D.S. van. (2011). Oxidative decarboxylation of unsaturated fatty acids. *Eur. J. Lipid Sci. Technol*, **113**:562–571.

Knothe, G. J. (2000). Monitoring a progressing transesterification reaction by fiber-optic near infrared spectroscopy with correlation to ^{1}H nuclear magnetic resonance spectroscopy. *Am. Oil Chem. Soc*, **77**: 489-493.

Knothe, G. (2006). Analysis of oxidized biodiesel by ^{1}H-NMR and effect of contact area with air. *Eur. J. Lipid Sci. Technol*, **108**: 493- 500.

Kochi, J. K. (1965). The Mechanism of Oxidative Decarboxylation with Lead (IV) Acetate. *J. Am. Chem. Soc*, **87**: 1811-1812.

Kothe, G. (2005). Dependence of bio diesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process. Technol*, **86**: 1059−1070.

Lestari, S., Maki-Arvela, P., Simakova, I.L., Beltramini, J., Lu, G.Q.M., Murzin, D.Y. (2009). Catalytic deoxygenation of stearic acid and palmitic acid in semibatch mode. *Catal. Lett*, **130**:48-51.

Li, L., Coppola, E., Rine J., Miller, J. L., Walker, D. (2010). Catalytic Hydrothermal Conversion of Triglycerides to Non-ester Biofuels. *Energy & Fuels*, **24**: 1305–1315.

Lima, D. G., Soares, V.C.D., Ribeiro, E. B., Carvalho, D.A., Cardoso, E. C. V., Rassi, F. C., Mundim, K. C., Rubim, J. C. and Suarez, P. A. Z., J. (2004). Diesel-like fuel obtained by pyrolysis of vegetable oils. *Anal. Appl. Pyrolysis*, **71**: 987–996.

Lu, J., Behtash, S., and Heyden, A. (2012). Theoretical Investigation of the Reaction Mechanism of the Decarboxylation and Decarbonylation of Propanoic Acid on Pd (111) Model Surfaces. *J. Phys. Chem. C*, **116**:14328-14341.

Maher, K. D. and Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresour. Technol*, **98**:2351–2368.

Maier, W.F., Roth, W., Thies, I., V, Rague, Schleyer, P. (1982). Hydrogenlysis, IV. Gas phase decarboxylation of carboxylic acids. *Chem. Ber*, **115**:808-812.

Maki-Arvela, P., Kubickova, I., Snare, M., Eranen, K and Murzin, D.Y. (2007). Catalytic deoxygenation of fatty acids and their derivatives. *Energy fuels*, **21**:30-41.

Maki-Arvela, P., Snare, M., Eranen, K., Myllyoja, J., Murzin, D.Y. (2008). Continuous decarboxylation of lauric acid over Pd/C catalyst. *Fuel*, **87**:3543-3549.

Matsubara, S., Yokota, Y. and Oshima, K. (2004). Palladium-catalyzed decarboxylation and decarbonylation under hydrothermal conditions. Decarboxylative deterioration. *Org. Lett*, **6**:2071–2073.

Morgenstern, M., Cline, J., Meyer, S., Cataldo, S. (2006). Determination of the Kinetics of Biodiesel Production Using Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). *Energy & Fuels*, **20**: 1350-1353.

Murzin, D.Y., Kubickova, I., Snare, M., Maki-Arvela, P and Myllyoja, J. (2009). Method for the manufacture of hydrocarbons. US Patent Number 7491858.

Myllyoja, J., Aalto, P., Savolainen, P., Purola, P., Alopaeus, V. and Gronqvist, J. (2007). *US Pat*., US 2007/0010682 A1.

Nelson, L.A., Foglia, A., Marmer, W.N. (1996). Lipase-catalysed production of Biodiesel. *J. Am. Oil Chem. Soc*, **73**:1101-1195.

Neto, P. R. C., Caro, M. S. B., Mazzuco, L. M., Nascimento, M. G. J. (2004). Quantification of Soybean Oil Ethanolysis with ^{1}H NMR. *Am. Oil Chem. Soc*, **81**: 1111-1114.

Ramos, M. J., Fernandez, C. M., Casas, A., Rodriguez, L., Perez, A. (2009). Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresour. Technol*, **100**: 261−268.

Regalbuto, J. R. (2011). The sea change in US biofuels'funding: from cellulosic ethanol to green gasoline. *Biofuels, Bioprod. Bioref*, **5**:495–504.

Santillan-Jimenez, E., Crocker, M. (2012). Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation. *J. Chem. Technol. Biotechnol*, **87**:1041-1050.

Sebos, I., Matsoukas, A., Apostolopoulos, V. and Papayannakos, N. (2009). Catalytic hydroprocessing of cottonseed oil in petroleum diesel mixtures for production of renewable diesel. *Fuel*, **88**: 145–149.

Sharma, A., Verma, A., Luxami, V., Melo, J. S., D'Souza, S. F., Tejo Prakash, N., Prakash, R. (2013). New Proton Nuclear Magnetic Resonance-Based Derivation for Quantification of Alkyl Esters Generated Using Biocatalysis. *Energy & Fuels*, **27**:2660−2664.

Sheldon, R. A., Kochi, J. K. (2011). Oxidative Decarboxylation of Acids by Lead Tetra acetate. *Organic Reactions, Inc.,* DOI: 10.1002/0471264180.or019.04.

Shonetta, D.G., Jeffrey, W. F., Michael, G. B. (2006). A review of analytical methods for the identification and quantification of hydrocarbons found in jet propellant 8 and related petroleum based fuels. *Biomed. Chromatogr*, **20**: 492–507.

Silverstein, R. M., Bassler, G. C., Morril, T. C. (2005). Spectrometric Identification of Organic Compounds, 7th ed.; John Wiley & Sons: New York, pp 165-202.

Silva, C. L. M. (2005). Obtencüao de Esteres Etılicos a Partir da Transesterificacüao do Oleo de Andiroba com Etanol. M.S. Thesis, University of Campinas, Campinas, SP, Brazil.

Simakova, I., Simakova, O., Maki-Arvela, P. and Murzin, D. Y. (2010). Decarboxylation of fatty acids over Pd supported on mesoporous carbon. *Catal. Today*, **150**:28–31.

Simakova, I.L., Simakova, O.A., Maki-Arvela, P., Simakov, A., Estrada, M., Murzin, D.Y. (2009). Deoxygenation of palmitic and stearic acid over supported Pd catalysts: effect of metal dispersion. *Appl. Catal. A*, **355**:100-108.

Simakova, I.L., Simakova, O.A., Romanenko, A.V., Murzin, D.Y. (2008). Hydrogenation of vegetable oils over Pd on nanocomposite carbon catalysts. *Ind. Eng. Chem. Res*, **47**:7219-7225.

Snare, M., Kubickova, I., Maki-Arvela, P., Chichova, D., Ernanen, K and Murzin, D.Y. (2008). Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. *Fuel*, **87**:933-945.

Snare, M., Kubickova, I., Maki-Arvela, P., Eranen, K. and Murzin, D. Y. (2006). Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel. *Ind. Eng. Chem. Res*, **45**:5708–5715.

Sotelo-Boyaa´s R., Liu, Y. and Minowa, T. (2011). Renewable Diesel Production from the Hydrotreating of Rapeseed Oil with Pt/Zeolite and NiMo/Al_2O_3 Catalysts *Ind. Eng. Chem. Res*. **50**:2791–2799.

Stefan, A.W. Hollak., Johannes, H. Bitter., Jacco van Haveren., Krijn, P. de Jong and Daan, S. van Es. (2012). Selective deoxygenation of stearic acid via an anhydride pathway. *RSC Adv*, **2**:9387–9391.

Stumborg, M., Wong, A. and Hogan, E. (1996). Hydro processed vegetable oils for diesel fuel improvement. *Bioresour. Technol*, **56**:13–18.

Suppes, G. J., Bockwinkel, K., Lucas, S., Botts, J. B., Mason, M. H., Heppert, J. A. (2001). Calcium Carbonate Catalyzed Alcoholysis of Fats and Oils. *J. Am. Oil Chem. Soc.*, **78**:139-146.

Wilberg, K. B. (1965). Oxidation in Organic Chemistry. *Academic Press*, New York.

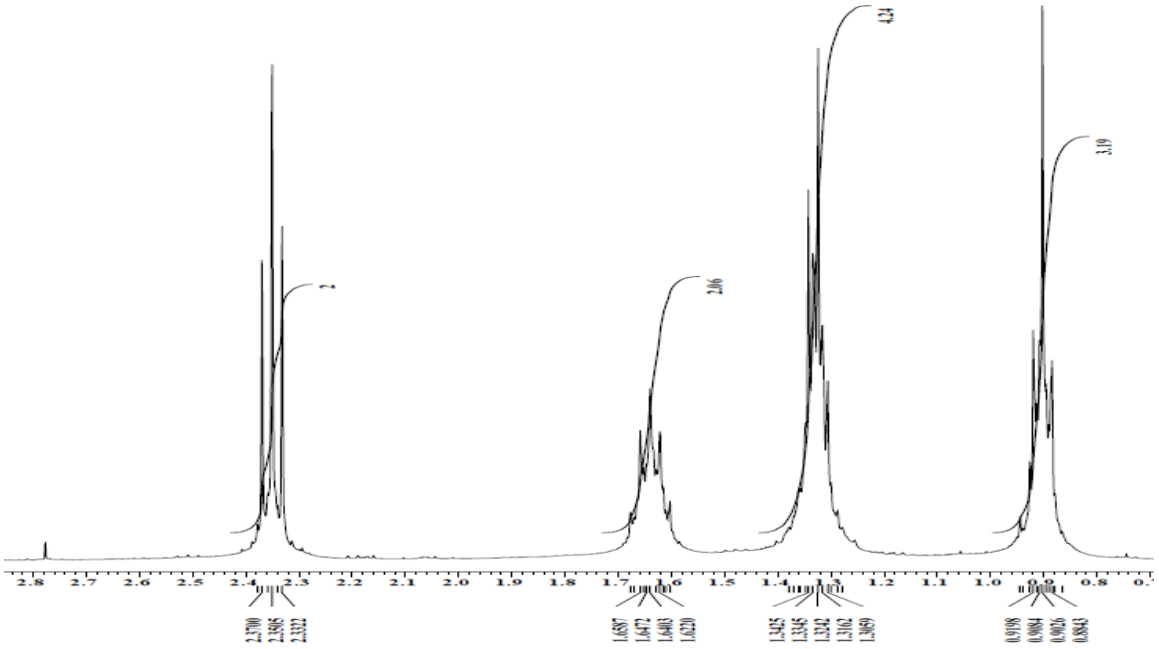


Figure 1- ^{1}H NMR of decarboxylation product of Hexanoic acid with silver nitrate.

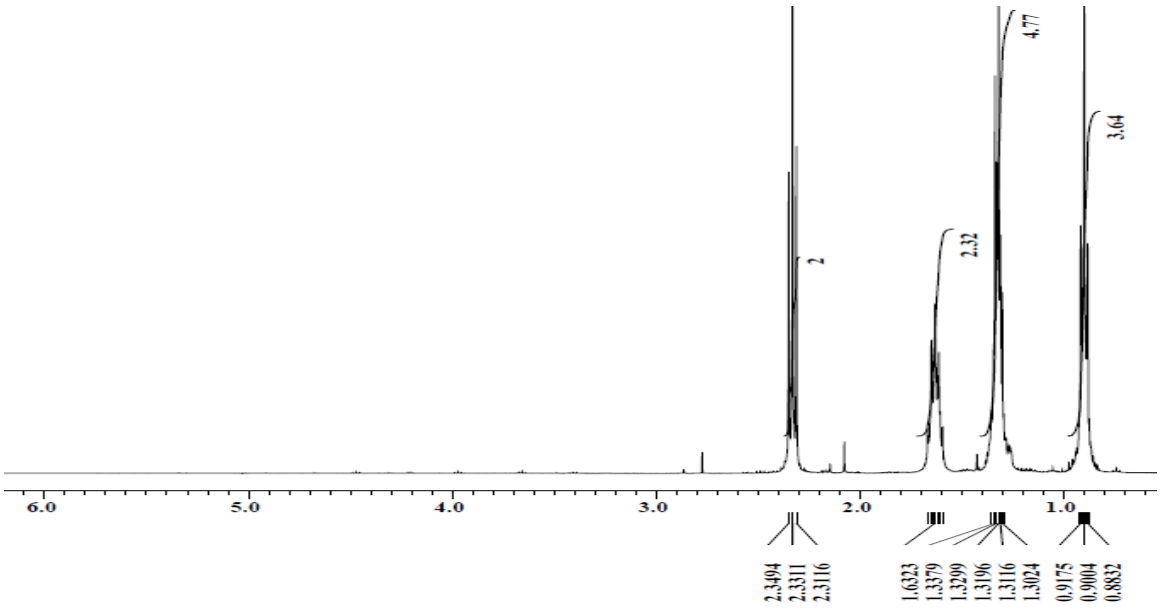


Figure 2- ^{1}H NMR of decarboxylation product of Hexanoic acid with lead (II) acetate.

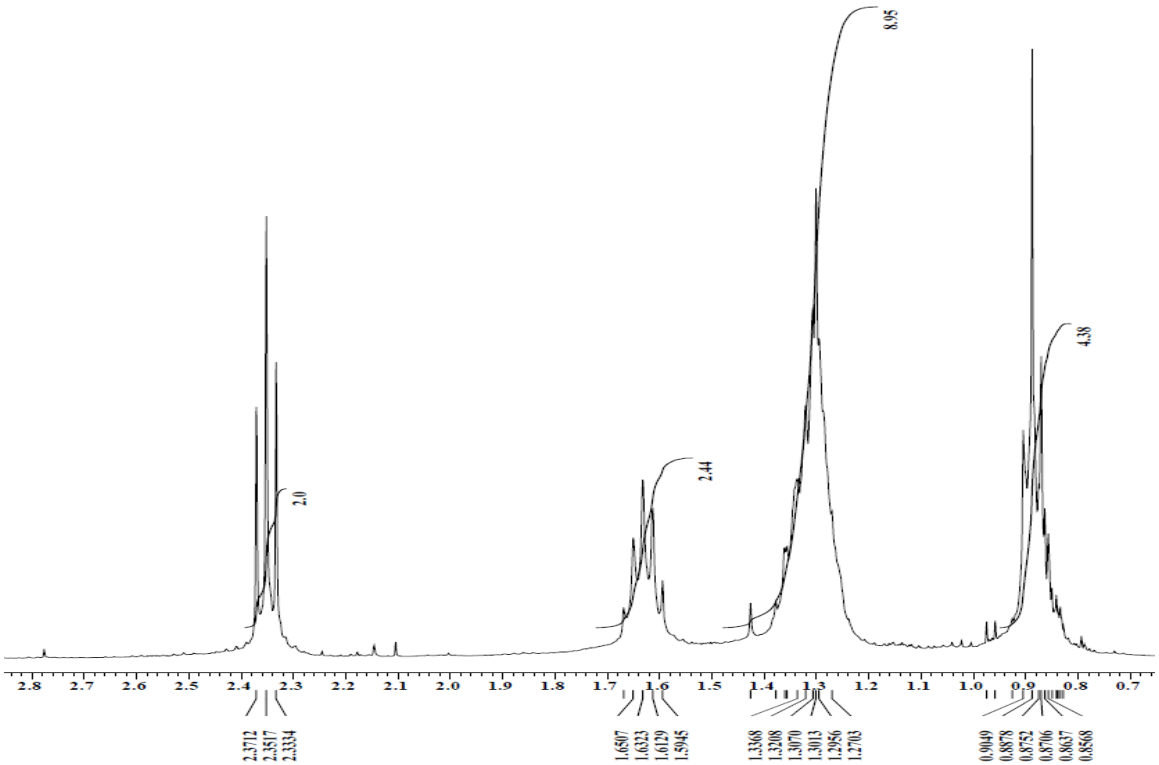


Figure 3- ^{1}H NMR of decarboxylation product of Heptanoic acid with silver nitrate.

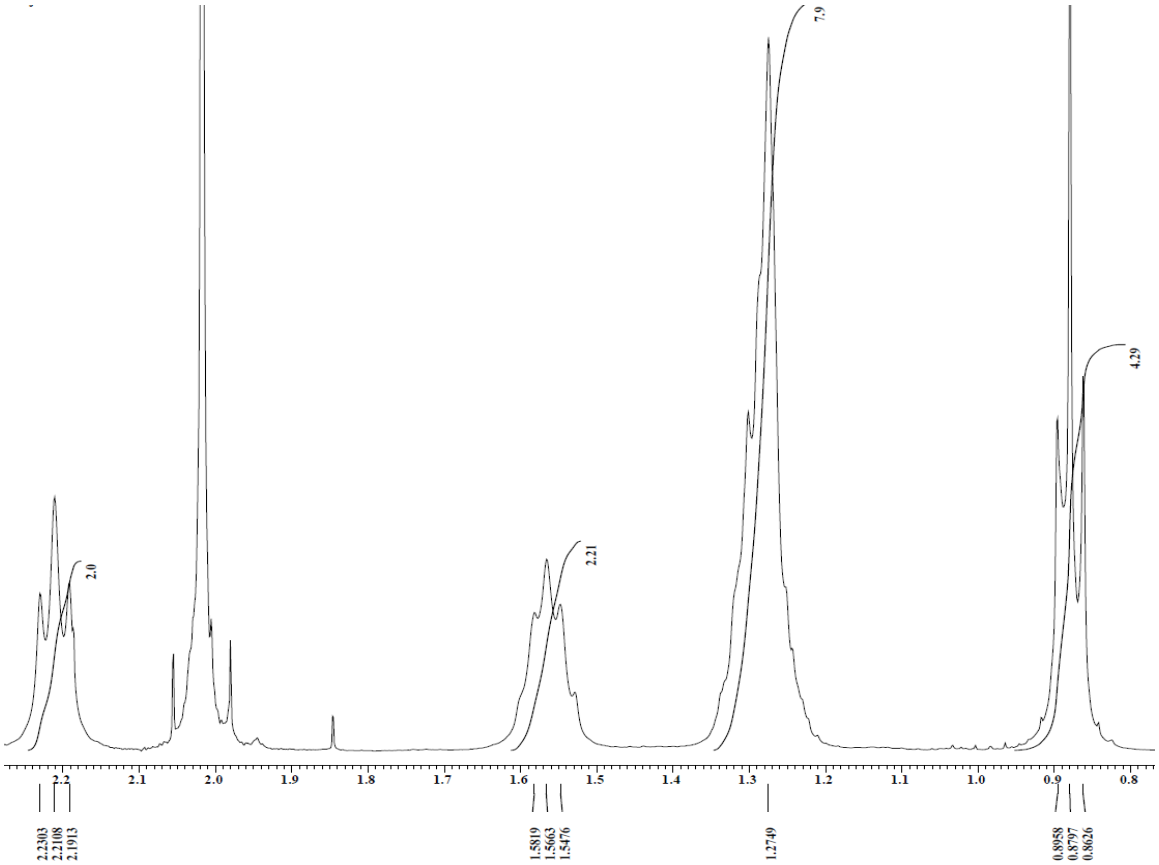


Figure 4- ^{1}H NMR of decarboxylation product of Heptanoic acid with lead (II) acetate.

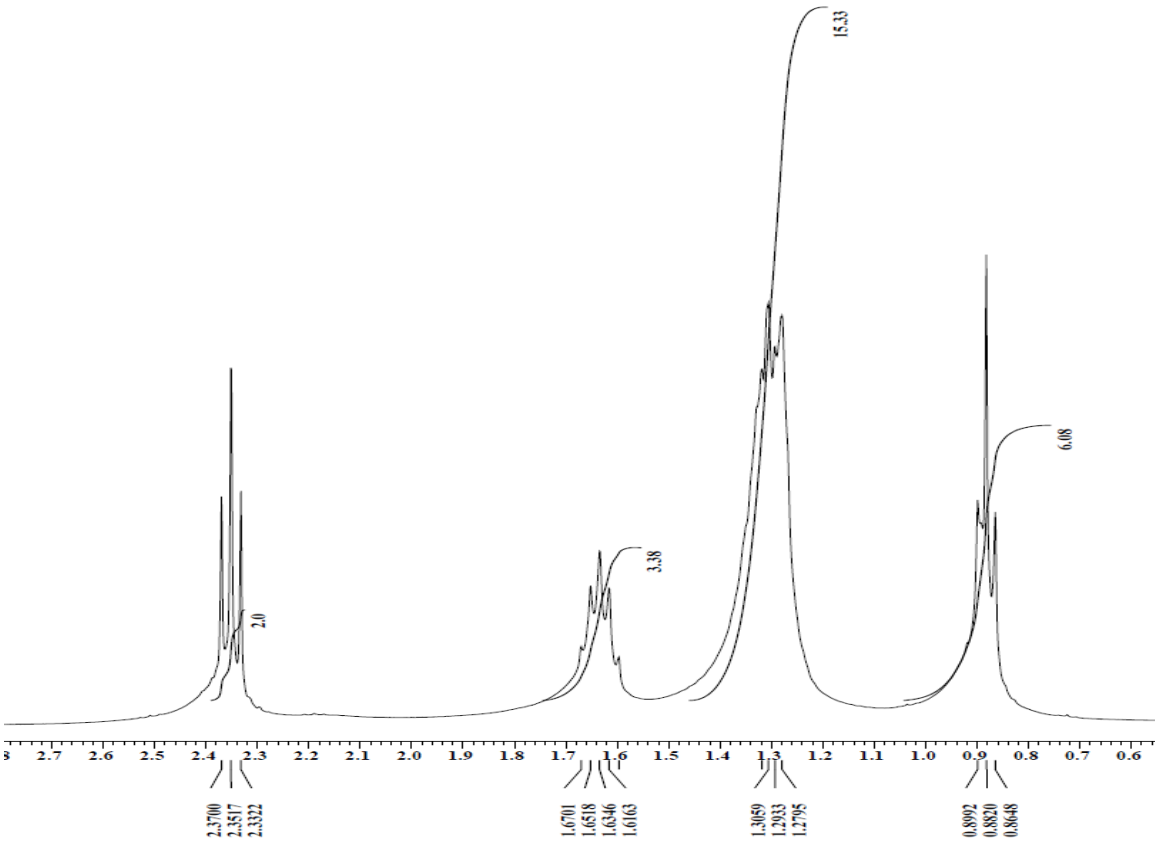


Figure 5- ^{1}H NMR of decarboxylation product of Octanoic acid with silver nitrate.

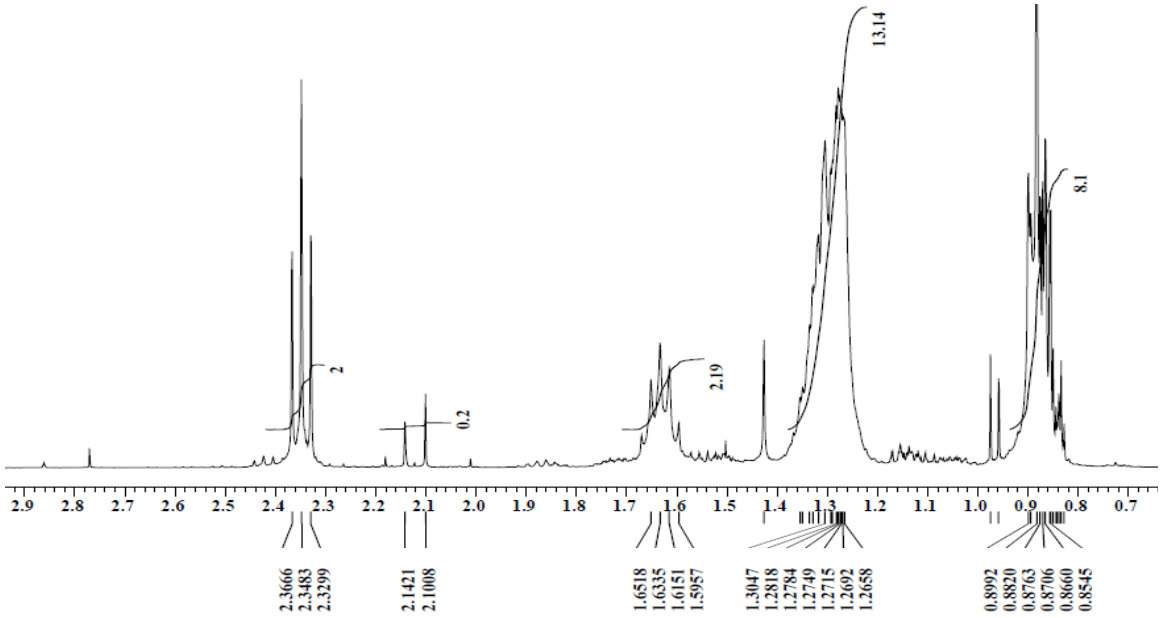


Figure 6- ^{1}H NMR of decarboxylation product of Octanoic acid with lead (II) acetate.

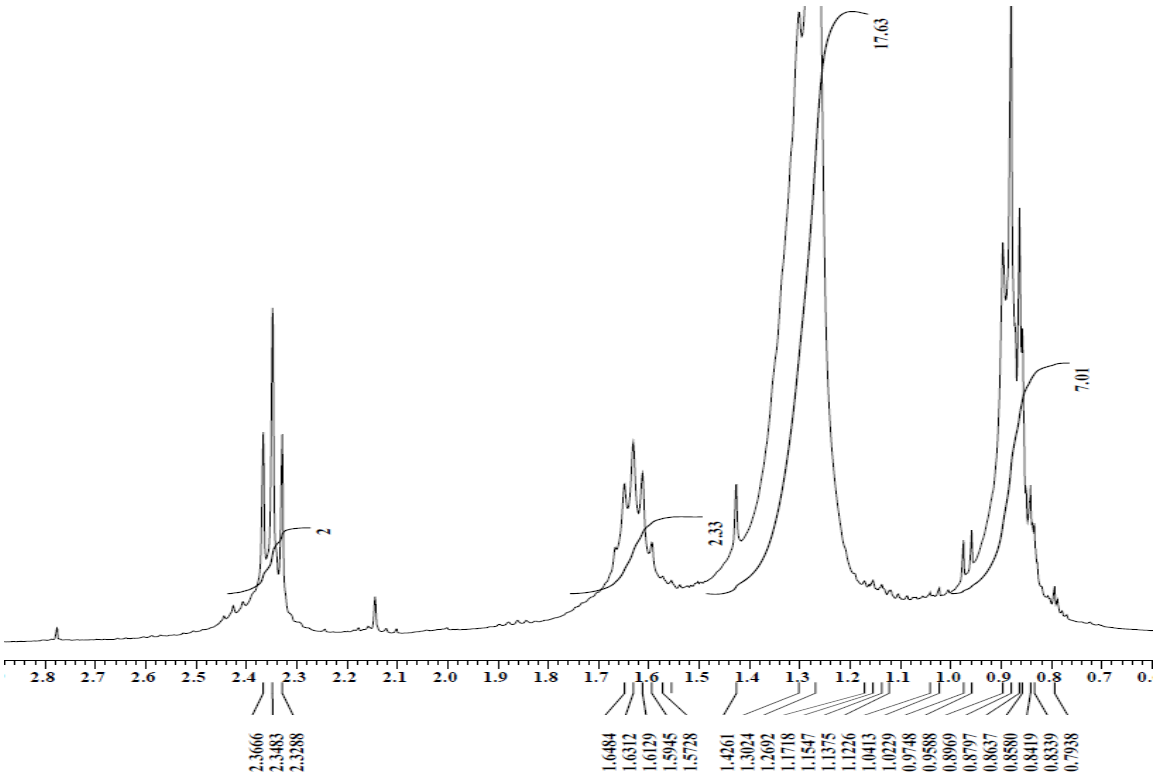


Figure 7- ^{1}H NMR of decarboxylation product of Decanoic acid with silver nitrate.

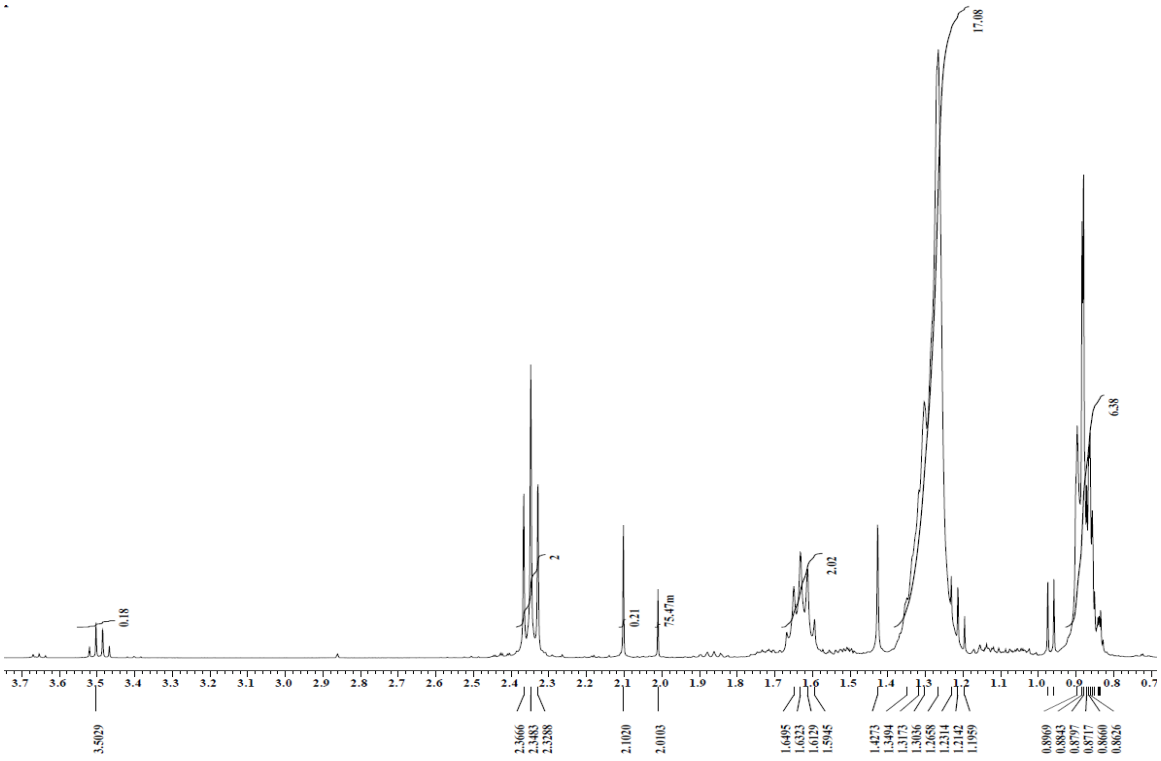


Figure 8- ^{1}H NMR of decarboxylation product of Decanoic acid with lead (II) acetate.

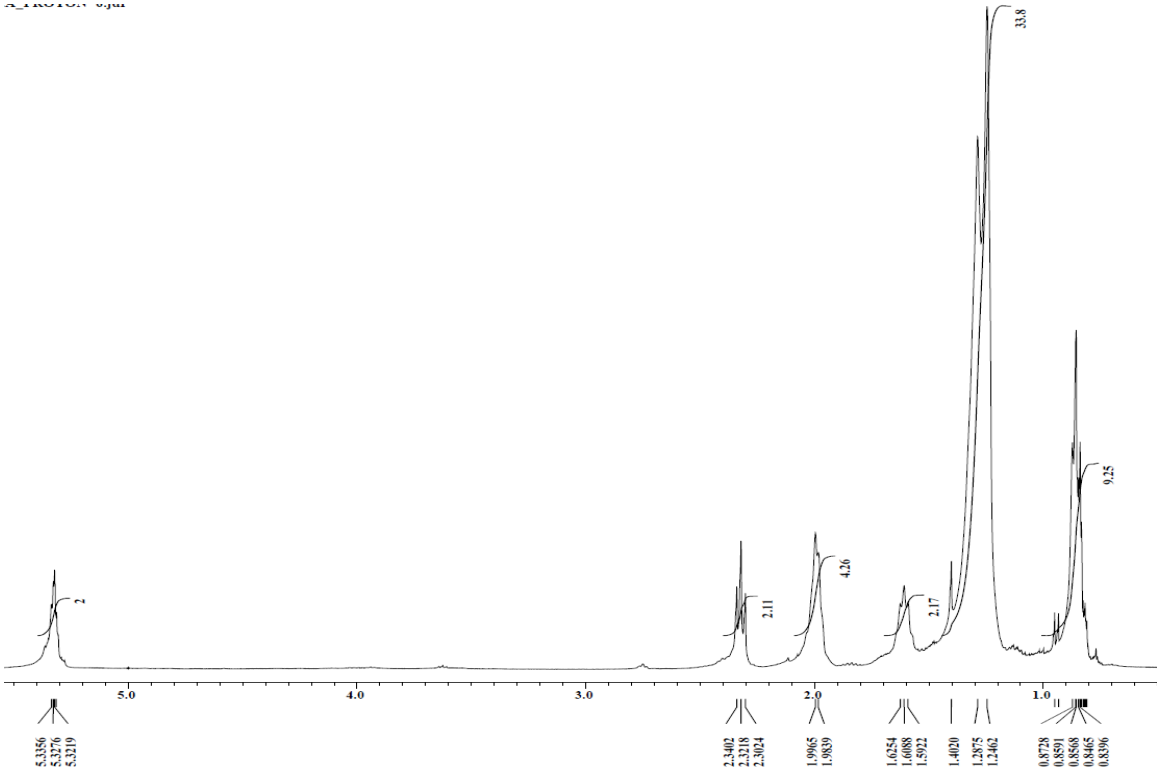


Figure 9- ^{1}H NMR of decarboxylation product of Oleic acid with silver nitrate.

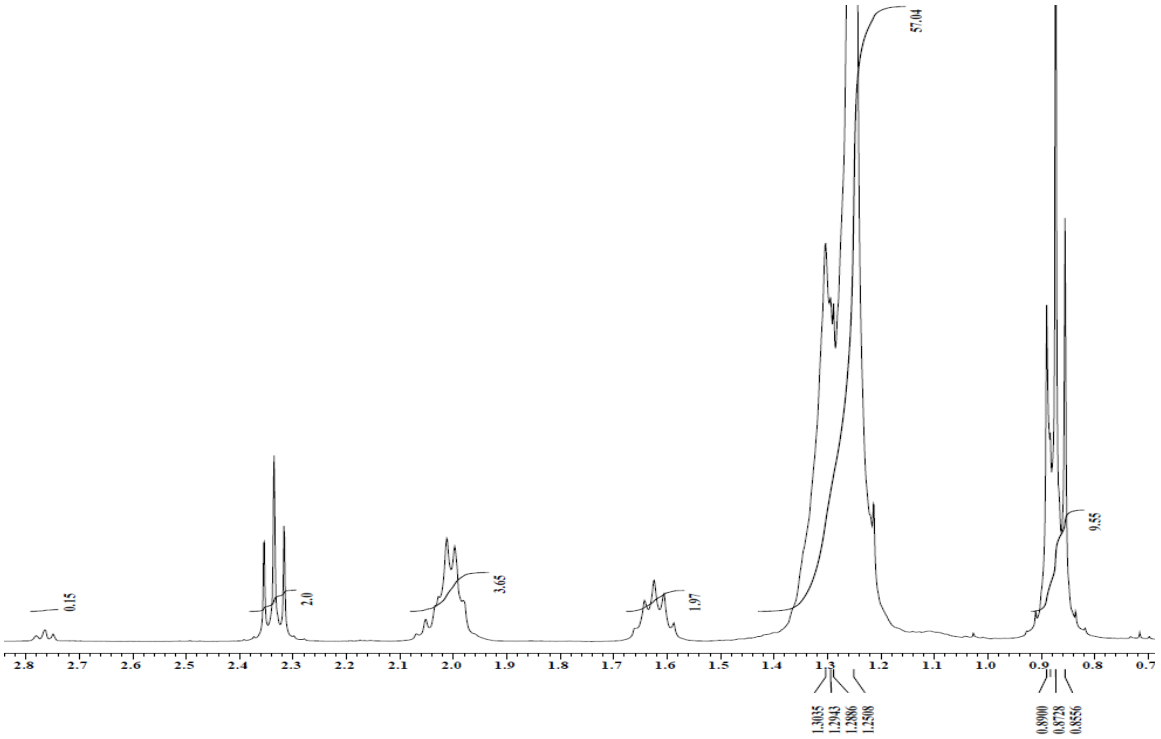


Figure 10- ^{1}H NMR of decarboxylation product of Oleic acid with lead (II) acetate.

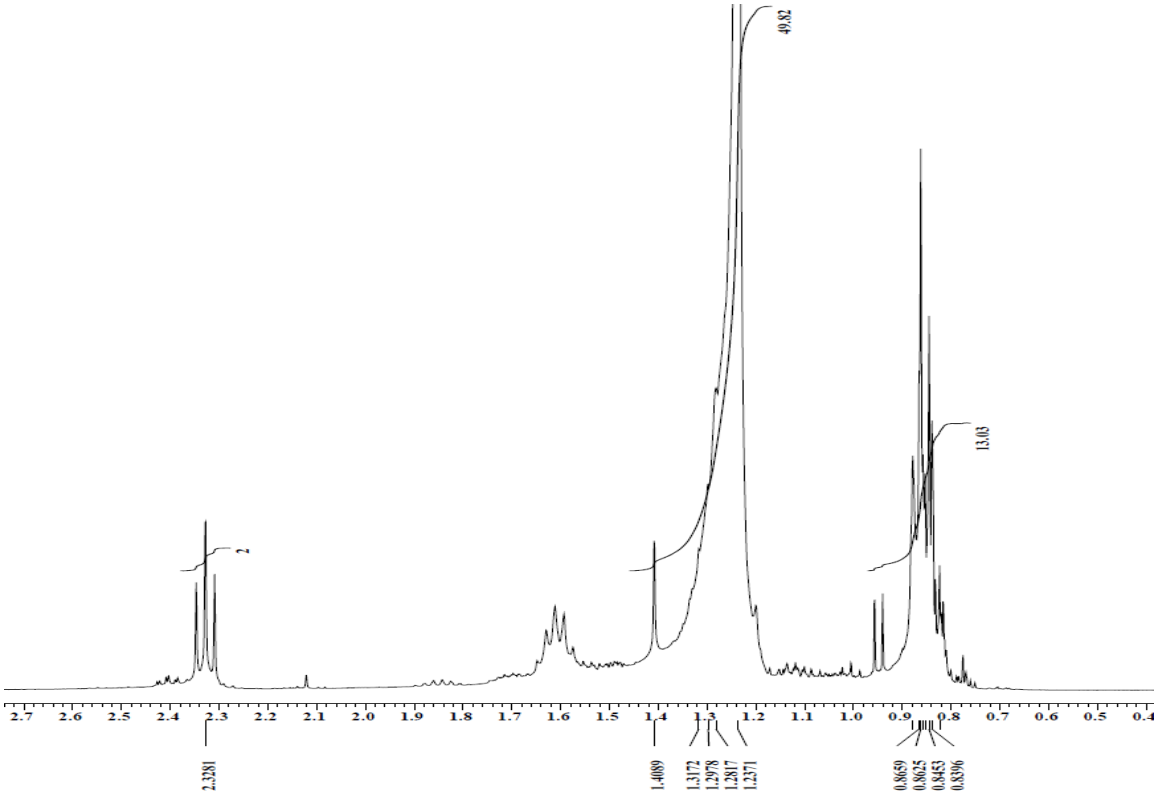


Figure 11- ^{1}H NMR of decarboxylation product of Palmitic acid with silver nitrate.

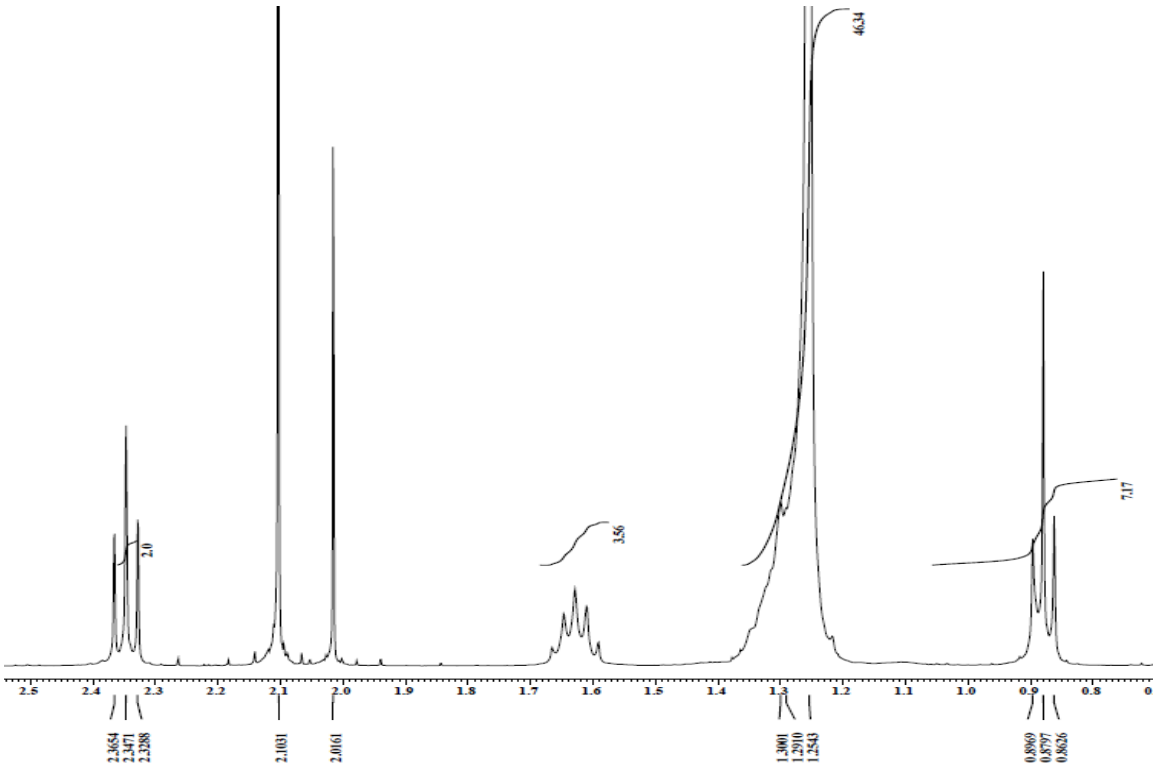


Figure 12- ^{1}H NMR of decarboxylation product of Palmitic acid with lead (II) acetate.

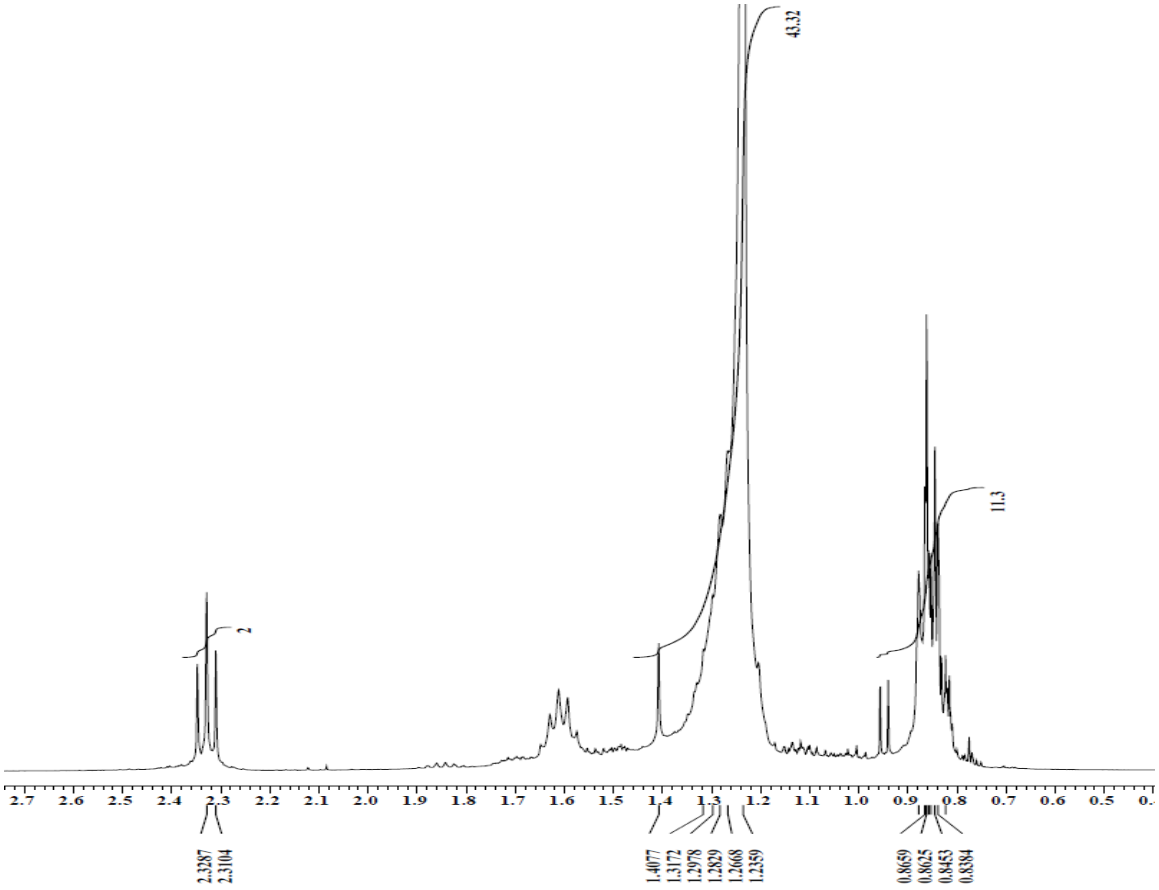


Figure 13- ^{1}H NMR of decarboxylation product of Stearic acid with silver nitrate.

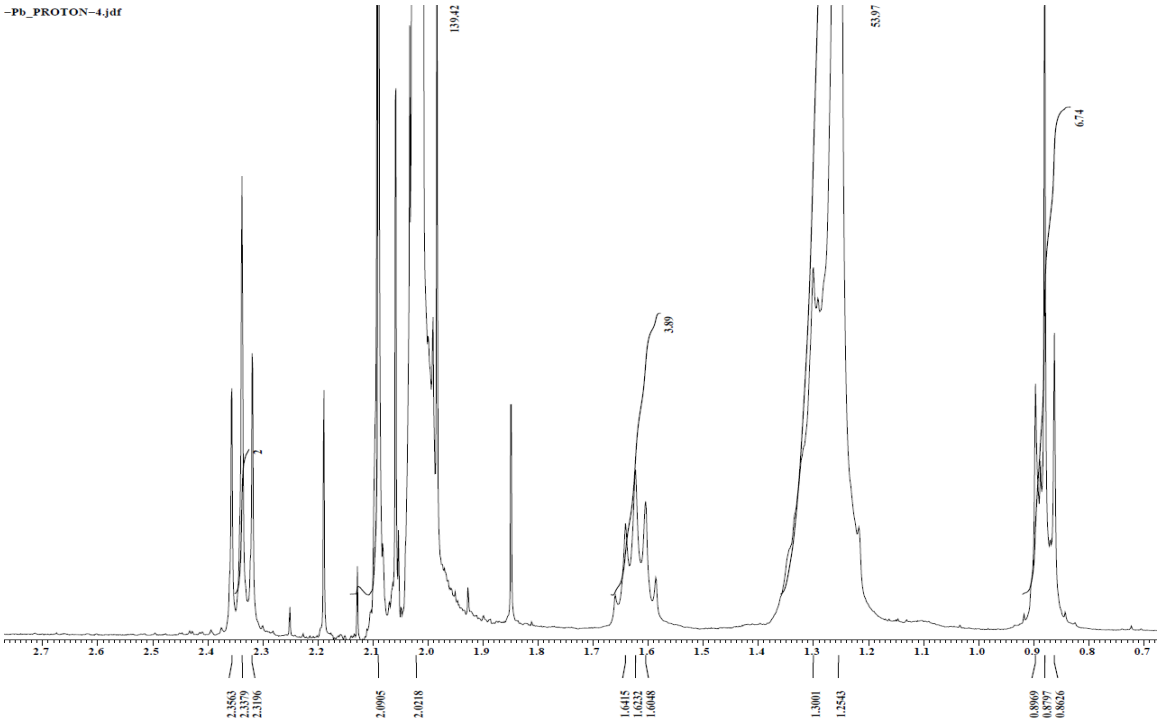


Figure 14- ^{1}H NMR of decarboxylation product of Stearic acid with lead (II) acetate.

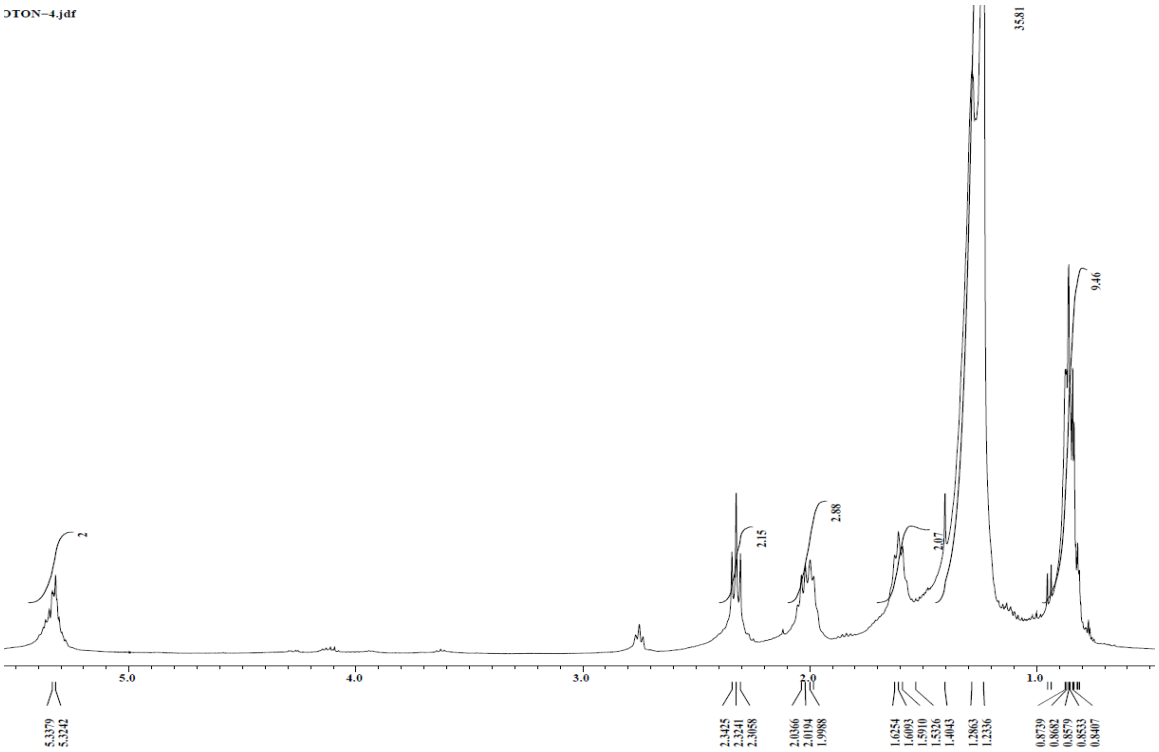


Figure 15- ^{1}H NMR of decarboxylation product of Cotton seed oil with silver nitrate.

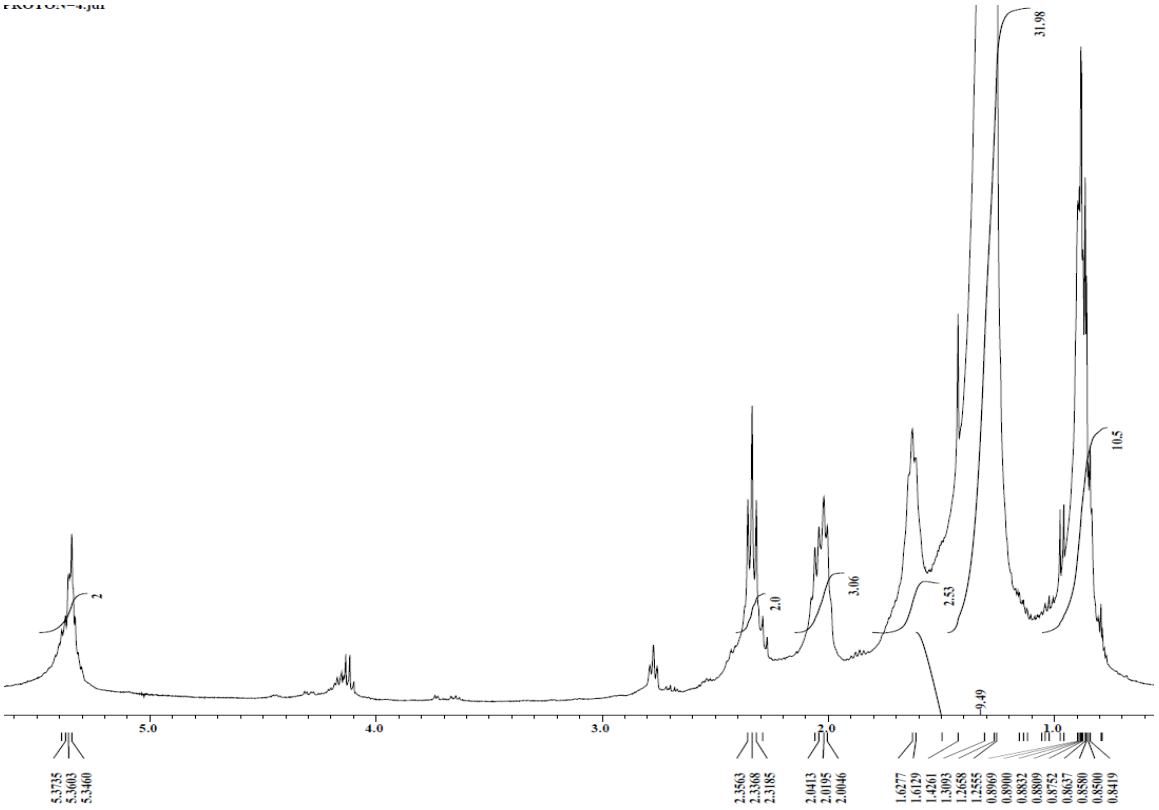


Figure 16- ^{1}H NMR of decarboxylation product of Cotton seed oil with lead (II) acetate.

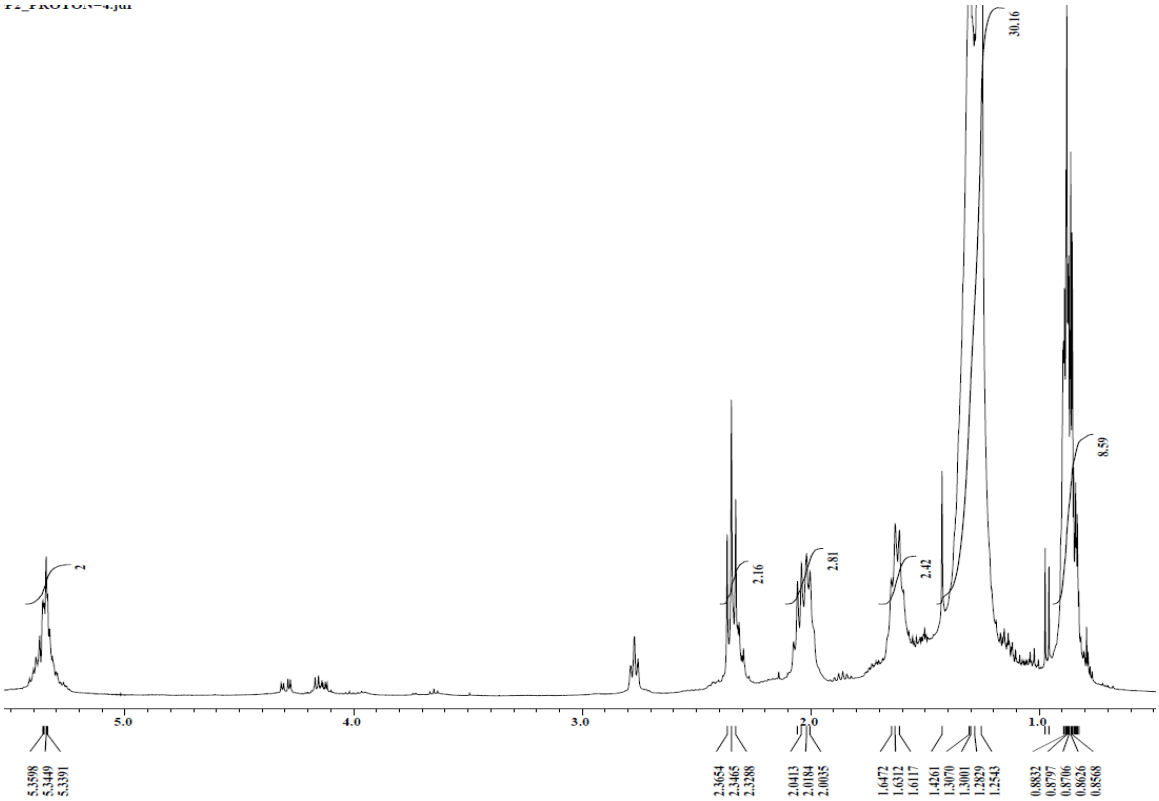


Figure 17- ^{1}H NMR of decarboxylation product of Rice bran with silver nitrate.

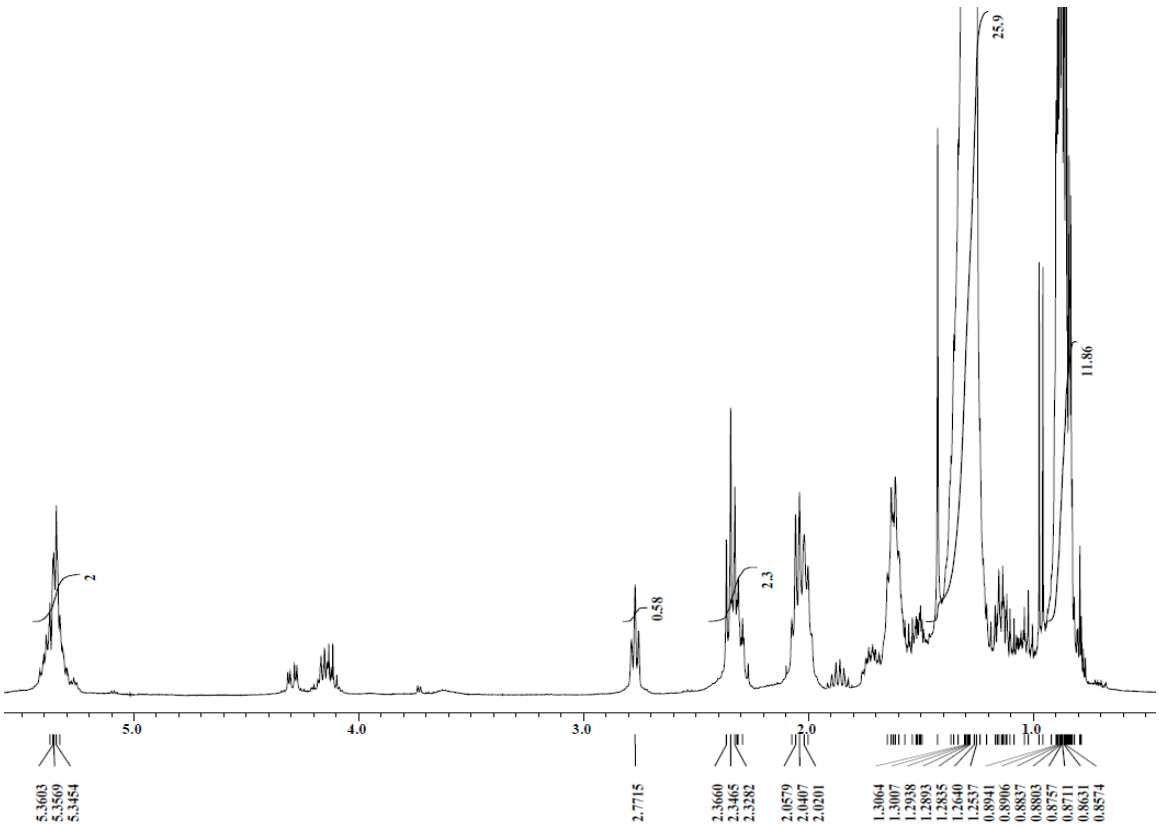


Figure 18- ^{1}H NMR of decarboxylation product of Rice bran with lead (II) acetate.

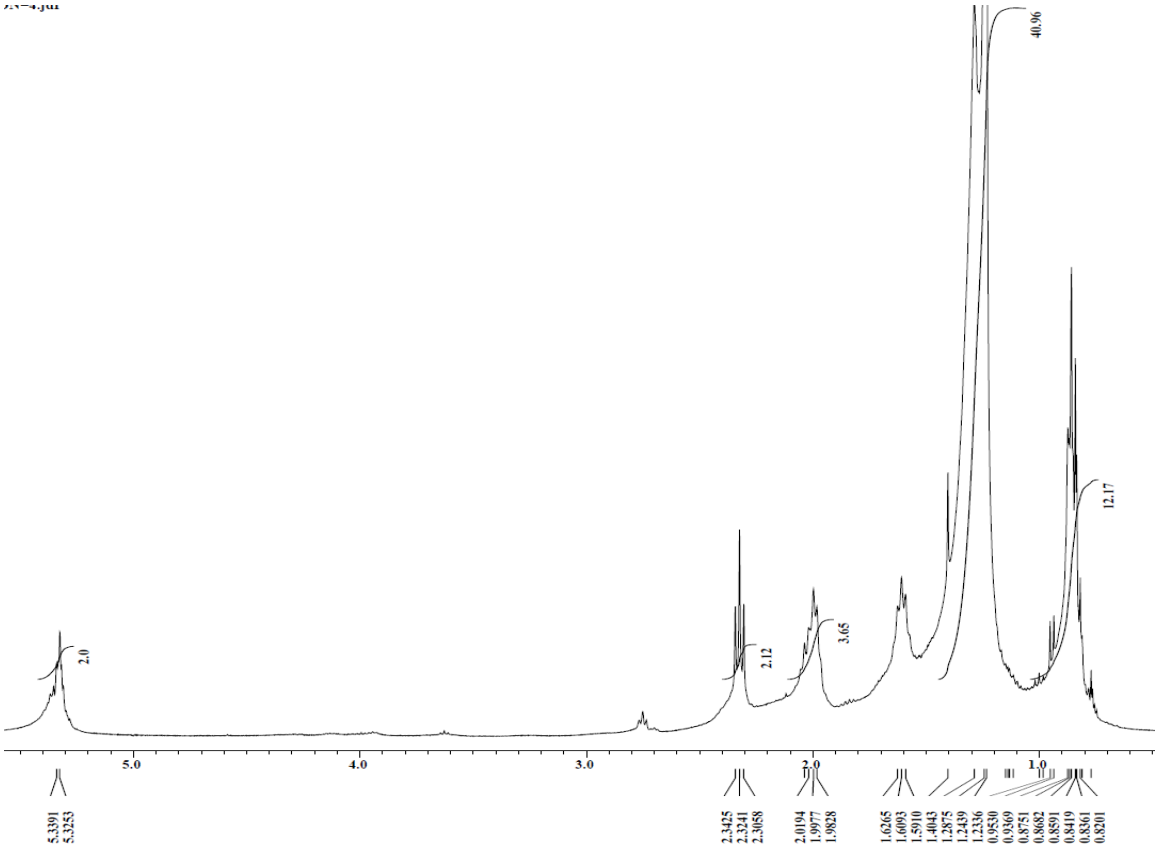


Figure 19- ^{1}H NMR of decarboxylation product of Ground nut with silver nitrate

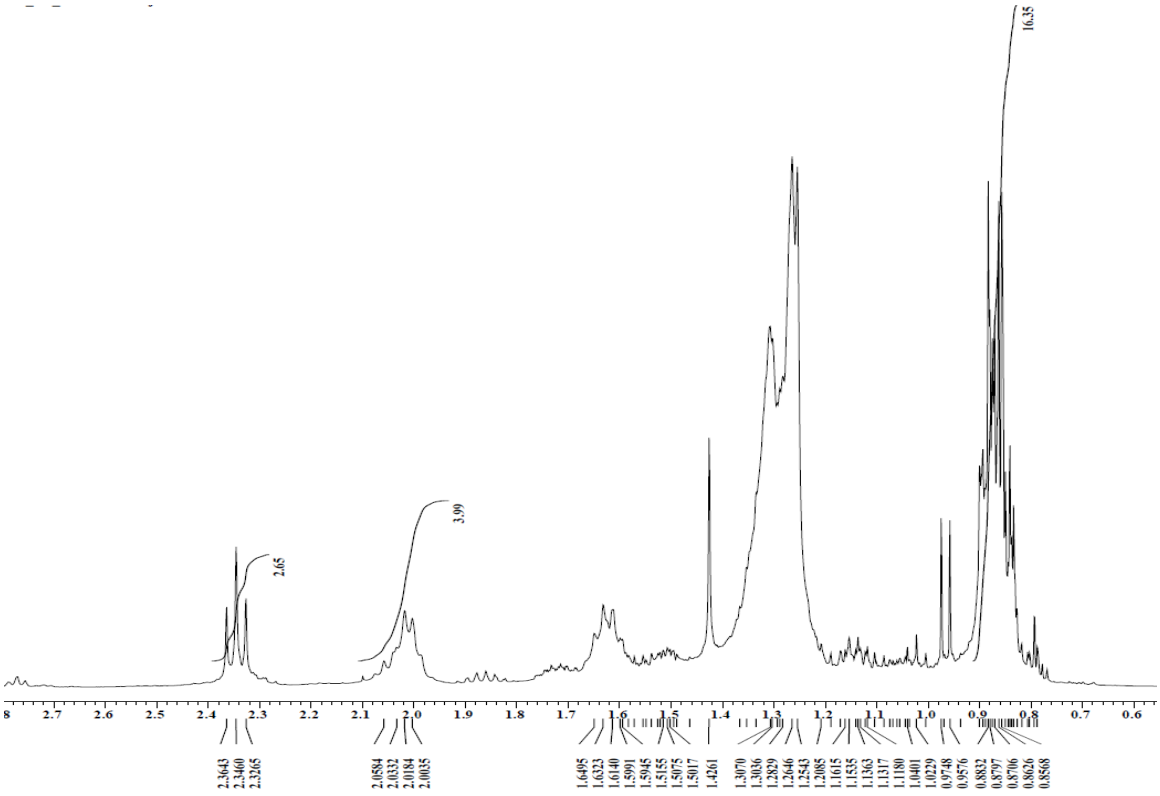


Figure 20- ^{1}H NMR of decarboxylation product of Ground nut with lead (II) acetate.