Mixed oxides as heterogeneous catalysts for transesterification reaction

A

Thesis submitted
In partial fulfilment for
the Award of the degree of
Master of Science in Chemistry

Submitted by:
Ms. Richa Aggarwal
(Reg. No. 300802015)

Under the Supervision of:
Dr. Satnam Singh
Assistant Professor

School of Chemistry and Biochemistry
THAPAR UNIVERSITY, PATIALA-147004

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Richa Aggarwal

Richa Aggarwal

Candidate's Declaration

I hereby declare that the work presented in the thesis entitled **"Mixed oxides as heterogeneous catalysts for the transesterification"** in partial fulfilment of the requirement for the award of the degree of Masters of Science in Chemistry and being submitted to Thapar University, Patiala, in my own work during the period of January 2010 to June 2010, under the supervision of Dr. Satnam Singh, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the contents embodied in this thesis for the award of any other degree.

Richa Aggarwal

Patiala
Date: 15 July 2010

Richa Aggarwal

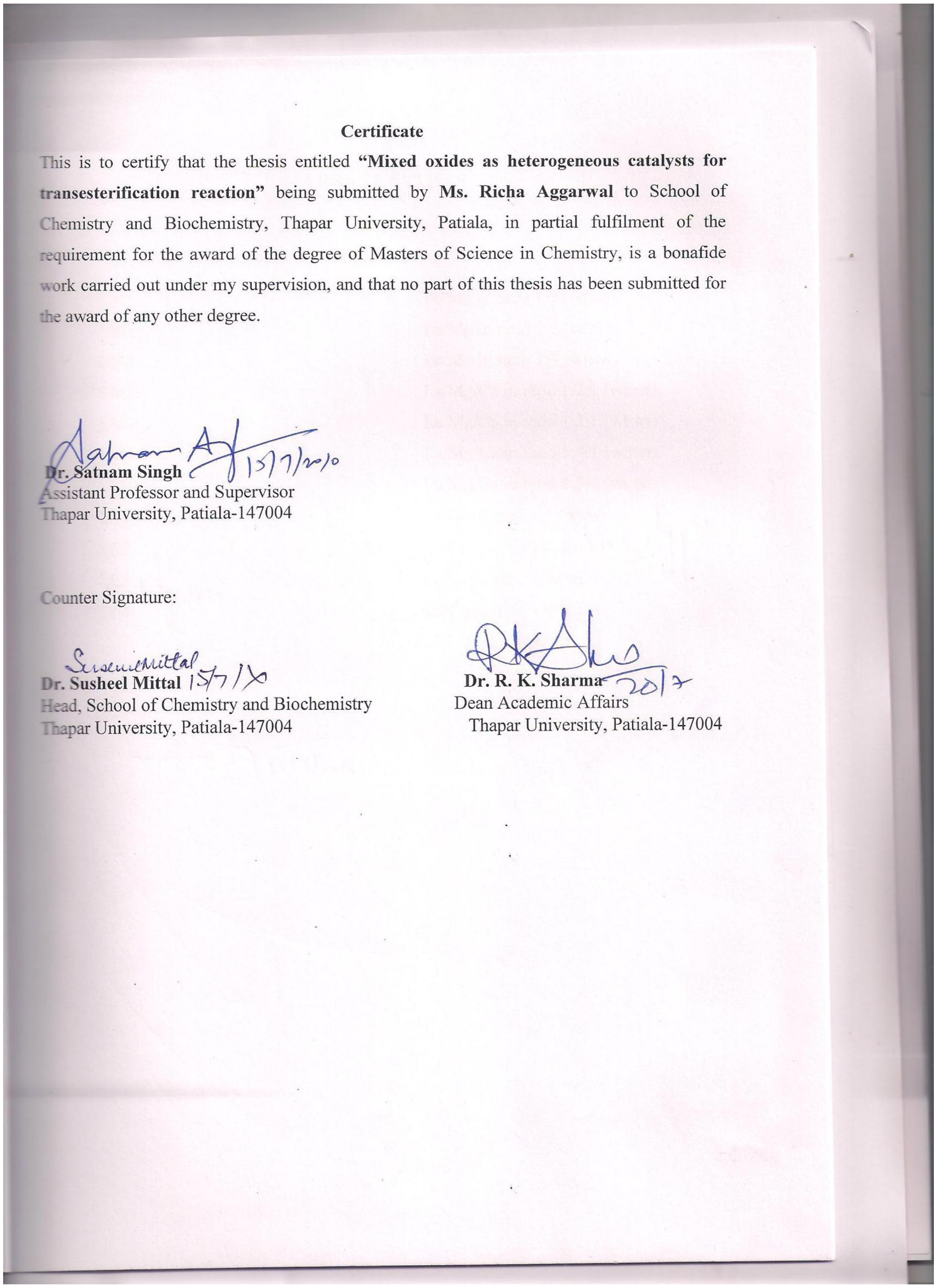
This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

15/7/2010

Dr. Satnam Singh
Assistant Professor and Supervisor,
School of Chemistry and Biochemistry
Thapar University, Patiala-147004

Susheel Mittal 15/7/10

Dr. Susheel Mittal
Head,
School of Chemistry and Biochemistry,
Thapar University, Patiala-147004



Certificate

This is to certify that the thesis entitled **"Mixed oxides as heterogeneous catalysts for transesterification reaction"** being submitted by **Ms. Richa Aggarwal** to School of Chemistry and Biochemistry, Thapar University, Patiala, in partial fulfilment of the requirement for the award of the degree of Masters of Science in Chemistry, is a bonafide work carried out under my supervision, and that no part of this thesis has been submitted for the award of any other degree.

15/7/2010
Dr. Satnam Singh
Assistant Professor and Supervisor
Thapar University, Patiala-147004

Counter Signature:

SusheelMittal
Dr. Susheel Mittal 15/7/10
Head, School of Chemistry and Biochemistry
Thapar University, Patiala-147004

Dr. R. K. Sharma 20/7
Dean Academic Affairs
Thapar University, Patiala-147004

ABBREVIATION

LM1	La/Mg in ratio 1:1 (wt:wt)
LM2	La/Mg in ratio 1:2 (wt:wt)
LM3	La/Mg in ratio 1:3 (wt:wt)
LM2C	La/Mg/Ca in ratio 1:2:1 (wt:wt)
LM3C	La/Mg/Ca in ratio 1:3:1 (wt:wt)
LM4C	La/Mg/Ca in ratio 1:4:1 (wt:wt)
LM5C	La/Mg/Ca in ratio 1:5:1 (wt:wt)
LC1	La/Ca in ratio 1:1 (wt:wt)
LC2	La/Ca in ratio 1:2 (wt:wt)
LC3	La/Ca in ratio 1:3 (wt:wt)
LC4	La/Ca in ratio 1:4 (wt:wt)

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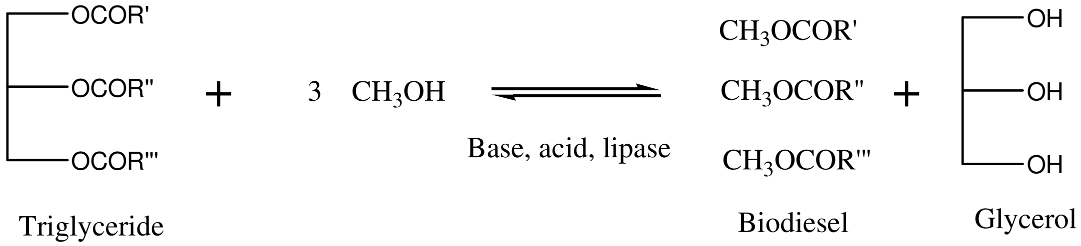
Abstract

Mixed oxides of La, Mg and Ca in three different combinations La/Mg, La/Ca and La/Mg/Ca with different weight proportions of elements were evaluated as catalysts for the transesterification of used cotton seed oil with methanol. These catalysts were characterized with Powder XRD, TEM, and Hammett indicator test. Among three combinations, La/Mg mixed oxides in all the studied proportion (La: Mg in 1:1, 1:2 and 1:3 wt/wt) were found to complete the transesterification of used cotton seed oil. La/Mg in 1:3 ratio was found to be efficient catalyst for the completion of the reaction in lesser time period. Hence, La/Mg in 1:3 ratios was studied for optimizing other parameters. An amount of 5 wt% of La/Mg catalyst (1:3) and oil: methanol molar ratio of 1:136 at reflux temperature were the optimum reaction parameters. All the studied proportions (1:2:1, 1:3:1, 1:4:1, 1:5:1 wt/wt) of La/Mg/Ca catalysts also catalyze the transesterification completely, but lesser reaction time was observed with 1: 4: 1 molar ratio. La/Ca mixed oxides (1:1, 1:2, 1:3, and 1:4 wt/wt) were found to be the less active catalysts in comparison to the La/Mg, La/Mg/Ca catalysts.

Introduction

The majority of world energy needs are supplied from Petrochemical sources like Coal and Natural gas. These sources are finite and non renewable and will be consumed shortly at current usage rates. Biodiesel, an alternative fuel for diesel engines and heating systems, can be produced by transesterification of the triglycerides with alcohols in the presence of catalyst (acid, alkali or enzymes) as shown in scheme 1.



Scheme 1

Biodiesel has become increasingly attractive because it is made from renewable sources and combines high performance with environmental benefits. It is a clean burning fuel, which is non toxic, biodegradable. Biodiesel is called environmentally friendly biofuel as it provides a means to recycle carbon dioxide. In other words, biodiesel does not contribute to global warming. Pure biodiesel do not emit sulphur, aromatic, particulates or carcinogenic compounds and is thus a safer alternative to petroleum diesel.

It can be used in mixed with petroleum diesel to produce a biodiesel blend that can be used in compression ignition engines under a variety of operating conditions. Biodiesel can be used in all conventional diesel engines, delivers similar performance and engine durability to petroleum diesel, and requires virtually no modifications in fuel handling and delivery systems. In addition, Biodiesel increases lubricity (even at blends as low as 3% or less), which prolongs engine life and reduces the frequency of engine part replacement.

Selection of the catalysts used in transesterification depends on the amount of free fatty acid (FFA) content present in the oil. If the FFA content of oil is high acid catalyzed esterification is followed by transesterification. On the other hand alkaline catalysts are less corrosive than acidic compounds and catalyze the reaction faster than acidic catalyst. Despite the industrial applicability, homogeneous catalyst has their own limitations. The catalyst dissolves fully in the glycerin layer and partially in biodiesel and result in contamination of biodiesel and glycerol (by-product) which requires additional step of neutralization by acid[1a]. Heterogeneous basic catalyst, on the other hand, greatly simplify the post treatment of the products (separation and purification) and can be easily separated from the system at the end of the reaction and may also be reused but this requires high temperature and pressure conditions. Hence these are more power consuming catalysts.

Utilization of lipase as a catalyst (Biocatalyst) for biodiesel production is a clean technology due to its non-toxic and environmentally friendly nature and requires mild operating conditions compared with chemical methods. But there are two bottlenecks in enzymatic approaches for biodiesel production: one is the relatively high cost of lipase and second its short operational life caused by the negative effects of excessive methanol and by-product glycerol.

In order to avoid the problem associated with homogenous catalyst and biocatalyst, there is need to develop less energy demanding heterogeneous catalytic systems. In the present work, mixed oxides of La, Mg, and Ca in three different combinations La/Mg/, La/Ca and La/Mg/Ca with different proportions of elements wt/wt were evaluated as catalysts for the transesterification of used cotton seed oil.

The homogeneous alkali – catalyzed transesterification is approximately 4000 times faster than acid catalysts. Mechanism of acid catalyzed and base catalyzed reaction is shown in Figure 2.1 and 2.2 respectively. In a base catalyze mechanism, alkali alkoxide species produced from alcohol and base generate a nucleophile RO^- which attacks on carbonyl carbon and resulting in the formation of tetrahedral intermediate. Tetrahedral intermediate breaks down into a fatty acid ester and a diglyceride anion. Then, proton transfer to the diglyceride ion regenerates the RO^- analytically active species.This sequence is then repeated twice to yield first a monoglyceride intermediate and finally the glycerol product and biodiesel.The key difference between the two reaction mechanisms is the strength of the nucleophilic attack on the carbonyl carbon of the FA. The nucleophile generated in the basic-catalyzed reaction (alkoxide ion) is significantly stronger than the alcohol nucleophile such that the formation of the FAME is significantly faster.

2.1. Acid catalysts

Homogeneous acid-catalyzed transesterification reaction requires non-green acids viz., sulfuric, phosphoric, hydrochloric and organic sulphonic acids as catalysts which works at higher reaction temperature and difficult to recycle [35-38]. This procedure seems to be more suitable when the feedstock is of low grade with relatively high FFA [39, 40] and/or moisture contents and when ethyl esters of fatty acids are to be obtained [35].

The development of solid acid catalysts has recently gained attention in view of their ease of separation and lack of corrosion or toxicity problems [28, 41and 42]. Unfortunately, the inorganic-oxide solid acids such as zeolite and niobic acid have low densities of effective acid sites and readily lose their activities under harsh conditions [43, 44]. Although strong acidic ion-exchange resins such as amberlyst and nafion have abundant sulphonic acid groups ($–SO_3H$) which act as strong acid sites but these resins are expensive and their catalytic activities are still much lower than that of sulfuric acid. In addition, such resins show low operational stability and their catalytic activity is lost after a few cycles of re-use [42, 45 and 46]. Sulfated zirconia, on the other hand, is an efficient solid acid catalyst [45, 47] but is expensive because zirconium is a rare and costly metal.

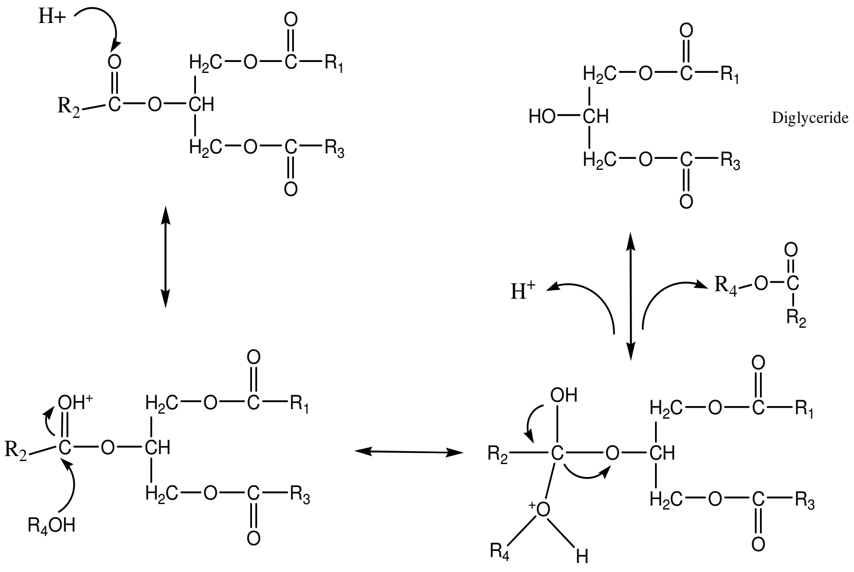


Figure 2.1: Acid Catalysed Reaction Mechanism

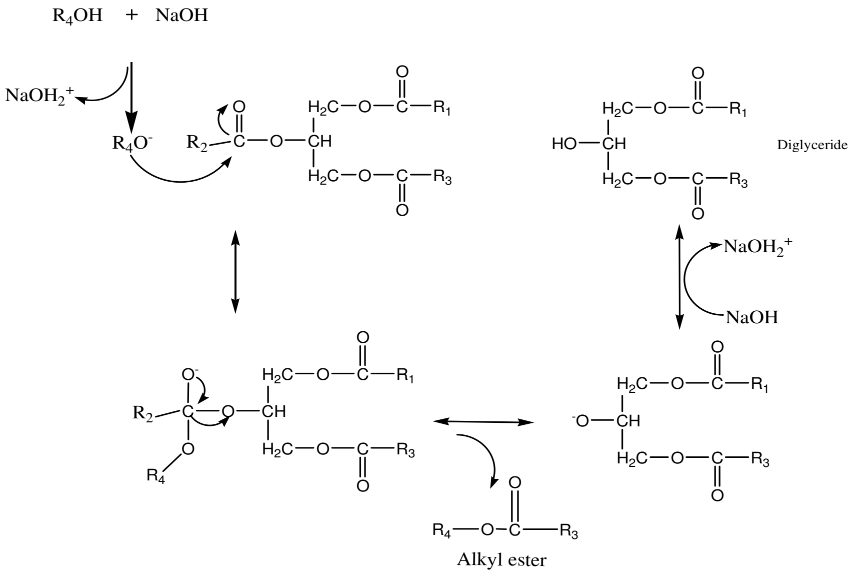


Figure 2.2: Base Catalysed Reaction Mechanism

2.2. Enzymatic catalyst

Enzymatic catalysts viz., lipases are able to catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems [48]. Although the lipases are non-polluting but they are usually expensive and methanol was found to denature the enzyme and decreasing its activity [34, 49-54]. Enzymes have shown good tolerance for the free fatty acid level of the feedstock, but are unable to provide the degree of reaction completion required to meet the ASTM fuel specification [55, 56].

2.3. Basic catalysts

Homogenous alkali-catalyzed transesterification can achieve more than 99% pure biodiesel within an half hour of reaction period provided FFAs and moisture contents of vegetable oil are less than 0.5% and 0.06% respectively [57]. Other basic catalyst used for transesterification includes carbonates and alkoxides of alkali metal ions and sodium methoxide was found to be more effective than sodium hydroxide, as small amount of water is expected to produce when sodium hydroxide is mixed with methanol [58]. However, homogenous alkali catalysts generally react with FFAs to form unwanted soap by-products leading to the deactivation of the catalyst [15].

More recently, there has been an increased research activity directed towards the development of heterogeneous catalyst systems for biodiesel production as they are easy to separate after the completion of the reaction, yield pure product and by product, easy to reuse, reduced corrosion problems and has low sensitivity to FFAs and water. Different heterogeneous catalysts used for transesterification are given below in table 2.1.

The fuel properties of the esters produced from the transesterification can vary depending on the types of vegetable oils used. Table 2.2 enlists fuel properties of methyl esters derived from different vegetable oils [79].

There is only one report by Lingaiah et al shows the use of mixed oxides of Mg and La for the transesterification of Sunflower, Jatropha, Soyabean and Ricebran oil [80].There is no report regarding use of mixed oxides of La/Mg/Ca for the transesterification. In present, mixed oxides of La/Mg and Ca in three different combinations La/Mg, La/Ca and La/Mg/Ca with different proportion of elements were evaluated as catalyst for the transesterification of used cotton seed oil.

Table 2.1: Different heterogeneous catalysts used for transesterification of vegetable oil

Vegetable oil	Catalysts	Molar ratio MeOH /Oil	Rxn time (h)	Temperature (^oC)	Conversion, %	Ref.
Blended Vegetable oil	Mesoporous silica loaded with MgO	8	5	220	96	[68]
Soybean oil	WO_3/ZrO_2, Zirconia-alumina and sulphated tin oxide	40	20	200-300	90	[64]
Soybean oil	La/Zeolite beta	14.5	4	160	48.9	[69]
Palm oil	$Mg–Al–CO_3$ (Hydrotalcite)	30	6	100	86.6	[65],[60]
Rapeseed oil	$CaTiO_3$, $CaMnO_3$,$Ca_2Fe_2O_5$, $CaZrO_3$, CaO-CeO_2	6	10	60	90	[71]
Soybean oil	$MgO.MgAl_2O_4$	3	10	65	57	[72]
Sunflower oil	CaO/SBA-14	12	5	160	95	[73]
Soybean oil	MgO, ZnO, Al_2O_3	55	7	70,100,130	82	[59]
Soybean oil	Cu and Co	5	3	70	-	[63]
Soybean oil	CaO, $Ca(OH)_2$, $CaCO_3$	-	2	65	99	[74]
Jatropha curcas oil	CaO	9	2.5	70	93	[75]
Rapeseed oil	Mg–Al	6	4	65	90.5	[67]
Soysbean oil	CaO, SrO	12	0.5-3	65	95	[77], [78]
Soybean oil	ETS-10	6	24	120	94.6	[62]
Cotton seed oil	$Mg–Al–CO_3$	6	12	180-210	87	[66]

Table 2.2: Fuel properties of methyl esters of vegetable oils [79]

Methyl ester of vegetables oil	Cetane number	Cloud point (^{o}C)	Pour point (^{o} C)	Flash point (^{o}C)	Density (kg/l)	Iodine value
Ground nut	54	5	-	176	0.883	95-121
Cotton seed	51	-	-4	110	-	-
Soybean	45	1	-7	178	0.885	120
Rapeseed	54	-2	-9	84	-	-
Babassu	63	4	-	127	0.875	60-68
Palm	62	13	-	164	0.880	69-94
Sunflower	49	1	-	183	0.860	122
Tallow	-	12	9	96	-	69-82
B20 (blend)	51	-	-16	128	0.859	-
Diesel	50	-	-16	76	0.885	-

OBJECTIVE

1) To prepare mixed oxide catalyst of La, Mg and Ca
2) To Study the transesterification reactions with prepared catalysts

Materials, Method and Experimental Work

This chapter deals with the materials used in the transesterification reaction, various methods used for the characterisation and the procedure of the reactions performed.

3.1 Materials and Method

Materials used:

Magnesium nitrate.6H_2O, lanthanum nitrate.6H_2O, calcium nitrate.4H_2O, KOH, K_2CO_3, methanol, hexane, ethyl acetate, silica gel, nitric acid, Buffer tablets of pH 4, 7 and 9.2, Ammonium chloride, ammonia solution, Deionised water, Hammett indicators viz., Phenolphthalien, Thymolphtallin, Alizarin and 2,4 – dinitroaniline of GR grade were obtained from Loba Chemicals Pvt. Ltd and used as such without further purification. Methanol (> 99%) was obtained from MERK, India. Used cotton seed oil was obtained from mess of hostle –I of Thapar University, Patiala.

Instruments

Powder XRD analytical X'pert with Ni-filtered Cu Kα radiation from Research & Development Centre of Thapar University, Patiala.

Transmission Electron Microscope (TEM) Hitachi (H-7500), with Image Analyser from Sophisticated Analytical Instrumentation Centre (SAIF), Punjab University, Chandigarh.

FT-NMR 400MHz Cryo Spectrometer (Bruker) from Sophisticated Analytical Instrumentation Centre (SAIF), Punjab University, Chandigarh.

3.2 Preparation of Catalyst

1. Mg/La Catalyst

Mixed oxides Mg/La Catalysts with different La/Mg ratio (1:1, 1:2, 1:3 wt/wt %) were prepared by coprecipitation at a pH 10 and used as catalysts for the transesterification. In a typical method of catalyst preparation, required amounts of $Mg(NO_3)_2.6H_2O$ and $La(NO_3)_3$ .6H_2O were dissolved in deionized water. The two precursor solutions were mixed homogeneously and allowed to precipitate using a basic solution of 1.0 M KOH and 0.25 M K_2CO_3 at a constant pH of 10. After ensuring complete precipitation, the precipitates were filtered and washed thoroughly with deionized water. The resultant catalyst mass was oven-dried at 120°C for 12 h and finally calcined at 650°C for 4 h. Prepared catalysts were designated as LM1, LM2, LM3 for La:Mg weight ratio of 1:1, 1:2, 1:3 respectively.

LM3 catalysts were also prepared at different pH 9.4, 9.5 and 10.5 with similar procedure and effect of pH on catalytic activity was studied with theses catalysts.

2. La/Mg/Ca Catalyst

In another series of catalysts having La/Mg/Ca with different La:Mg:Ca ratios (1:2:1, 1:3:1, 1:4:1 and 1:5:1 wt/wt %) were prepared by coprecipitation at a constant pH. In a typical method of catalyst preparation, required amounts of $Mg(NO_3)_2.6H_2O$, $La(NO_3)_3 .6H_2O$ and $Ca(NO_3) .4H_2O$ were dissolved in deionized water. The three precursor solutions were mixed homogeneously and allowed to precipitate using a basic solution of 1.0 M KOH and 0.25 M K_2CO_3 at a constant pH of 10. After ensuring complete precipitation, the precipitates were filtered and washed thoroughly with deionized water. The resultant catalyst mass was oven-dried at 120°C for 12 h and finally calcined at 650 °C for 4 h. These catalysts are designated as LM2C, LM3C, LM4C and LM5C for La: Mg: Ca weight ratios of 1:2:1, 1:3:1, 1:4:1 and 1:5:1 respectively.

3. La/Ca Catalyst

The catalysts La/Ca with different La/Ca ratios (1:2, 1:3, 1:4 wt/wt %) were prepared by coprecipitation at a constant pH. In a typical method of catalyst preparation, required amounts of $Ca(NO_3)_2.4H_2O$ and $La(NO_3)_3.6H_2O$ were dissolved in deionized water. The two precursor solutions were mixed homogeneously and allowed to precipitate using a basic solution of 1.0 M KOH and 0.25 M $K_2 CO_3$ at a pH of 10. After ensuring complete precipitation, the precipitate was filtered and washed thoroughly with deionized water. The resultant catalyst mass was oven-dried at 120 °C for 12 h and finally calcined at 650 °C for 4 h. The catalyst's designated as LC1, LC2, LC3 and LC4 having La/Ca ratios 1:1, 1:2, 1:3 and 1:4 wt/wt % respectively.

4. Transesterification

All of the transesterification reactions were performed in a 50 mL round-bottom flask equipped with a reflux condenser. In a typical reaction, the catalyst (5 wt%) was added to the stirring reaction mixture of oil (5g) and methanol (25g) at methanol reflux temperature (65°C) and progress of the reaction was monitored by thin-layer chromatography (Solvent system: hexane:ethyl acetate 24:1 (v/v)). Then selected catalyst was used to optimize various parameters viz., catalyst amount, methanol amount and reaction temperature.

3.3. Catalyst Characterisation

The physicochemical properties of all the prepared catalysts having different proportion of elements (wt/wt %) in three different types of combinations La:Mg, La:Mg:Ca, La:Ca were studied by various techniques ,viz powder XRD and TEM.

For Powder XRD , the measurements were recorded in steps of 0.0170° with a scan step time of 15.5 s and a 2θ range of 10–80°.TEM images of LM3 Catalyst prepared at pH 10 was taken. ^{1}H NMR Spectra of used Cotton Seed Oil and biodiesel were recorded.

The basic strength of all the prepared catalysts (H_) was determined using Hammett indicators. About 200 mg of catalyst was shaken with an appropriate volume of a methanol solution of Hammett indicator and left to equilibrate for 2 h to observe the colour change. In these experiments, the following Hammett indicators were used: phenolphthalein (H_8.2), Alizarin (H_11), Thymolphtallin (H_9.9) and 2,4-dinitroaniline (H_15). Basic strength of prepared catalyst is lying in the range near to pH of Hammett indicator when change in colour is observed for methanoic solution of same Hammett indicator.

3.4 Analysis of oil

Determination of Acid value of oil

Acid value was used to know the age and quality of oil. It is the number of milligrams of KOH required to neutralize the free fatty acid present in 1 g of oil.

When oil is stored, it may undergoes peroxide formation at the double bonds by atmospheric oxygen and hydrolysis by micro-organisms with liberation of free acid. Thus by calculating the free fatty acid present, we came to know about the purity of oil.

In order to study the acid content, 10 g of used cotton seed oil (one that has stood for several days at room temperature) was taken as sample and 1 ml of phenolphthalein was added to it. This was thoroughly mixed and titrated with 0.1 mol/litre of KOH until the pink colour persisted for 20-30 s. The number of millilitres of standard alkali required was calculated for the acid value of oil, given by the equation:

$$\text{Acid Value} = \frac{\text{Number of ml of KOH used}}{\text{Weight of the oil taken}} \times 5.6$$

Acid Value was found to be 0.385

Determination of Iodine value of oil

Across the double bonds of unsaturated fatty acids halogens could be added to form addition compounds. Iodine monochloride (ICl) was allowed to react with oil in the dark. The amount of iodine consumed was determined by titrating the iodine released (after the addition of KI) with standard Sodiumthiosulphate and comparing with a blank in which the oil was omitted. The reaction mixture was kept at dark and the titration was carried out as quickly as possible since halogens could be oxidised in the light.

In 10ml of oil, 25 ml of the ICl solution was added, shaken thoroughly (oil + ICl) and kept in dark for 1 h. In another blank set up cotton seed oil solution was replaced by 10 ml of chloroform (ICl + chloroform). Added 10ml of KI solution and titrated the released iodine with the standard thiosulphate. When the solution turned pale straw colour, added 1 ml of starch solution and continue titrating until the blue colour disappears. Bottle was shaken vigorously during titration to ensure that all the iodine is removed from the chloroform.

Difference in reading between blank (Bl) and test (T) that is (Bl-T) gives the number of 0.1 mol/litre thiosulphate needed to react with the equivalent volume of iodine. Since two molecules of thiosulphate are needed for each iodine, so now it becomes (Bl-T)/2.

The molecular weight of iodine is 2x127 so the weight of iodine in (Bl-T)/2 ml of 0.1mol/litre iodine was found to be

$$\frac{(\text{Bl-T}) \times 0.1 \times 2 \times 127}{2 \times 1000}\ \text{g}$$

The amount of oil taken is 0.2 g so the iodine value

$$\frac{(Bl\text{-}T) \times 12.7 \times 100}{0.2 \times 1000} \text{ g}$$

Iodine value = (Bl-T) x 6.35 g per 100 g of oil

Iodine value was found to be 89.50

Results and Discussion

4.1 Catalyst Characterization

4.1.1. Hammett indicator

Basic Strength of LM3, LMC1, LMC2, LMC3, LMC4, LMC5, LC1, LC2, LC3, LC4 catalysts were determined by Hammett indicators. It was observed that catalysts LM3 prepared at pH 10, 10.5 and LMC5 show sharp colour change of 2,4-dinitroaniline (H_15) where as all other catalysts showed the colour change of Alizarin (H_11). This shows that LM3 prepared at pH 10, 10.5 and LMC5 (pH 10) are more basic as compared to other prepared catalysts. In table 4.1 the basic strength of these catalysts are shown.

Table4.1: Basic strength of catalysts

Serial No.	Catalyst	pH for precipitation of catalyst	Hammett indicator (with highest possible basic strength) showing change of colour	Basic Strength
1	LM3	10	2,4-dinitroaniline	15<H_<18.0
2	LM3	10.5	2,4-dinitroaniline	15<H_<18.0
3	LM3	9.5	Alizarin	9.7<H_<11.0
4	LM3	9.4	Alizarin	9.7<H_<11.0
5	LM1C	10	Alizarin	9.7<H_<11.0
6	LM2C	10	Alizarin	9.7<H_<11.0
7	LM3C	10	Alizarin	9.7<H_<11.0
8	LM4C	10	Alizarin	9.7<H_<11.0
9	LM5C	10	2,4-dinitroaniline	15<H_<18.0
10	CL1	10	Alizarin	9.7<H_<11.0
11	CL2	10	Alizarin	9.7<H_<11.0
12	CL3	10	Alizarin	9.7<H_<11.0
13	CL4	10	Alizarin	9.7<H_<11.0

4.1.2. TEM images of LM3 catalyst

Transmission electron micrographs of catalyst LM3 prepared at pH 10 are shown in Fig 4.1(a), (b) & (c). It can be seen average particle size of the catalyst is in the range of 7-10 nm.

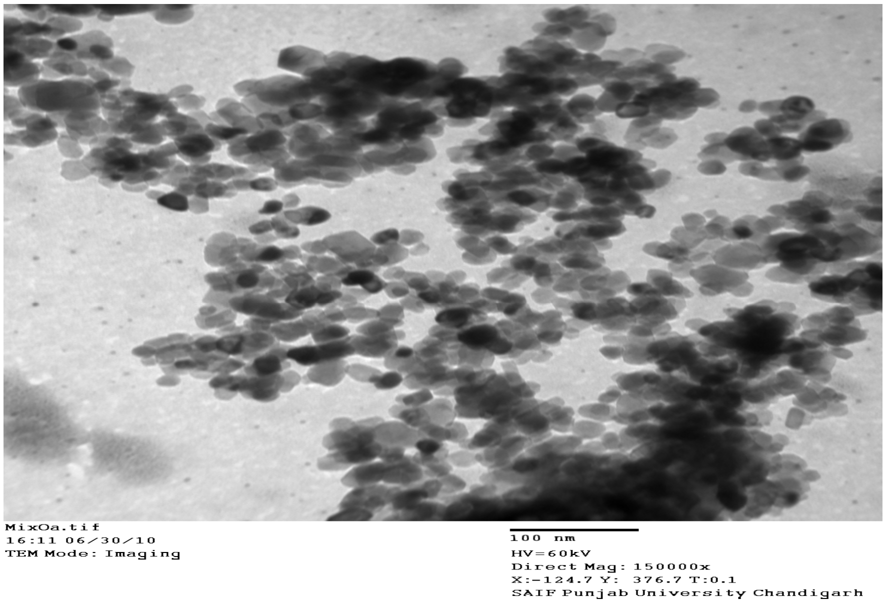


Figure 4.1(a): TEM image of LM3 catalyst prepared at pH 10

Figure 4.1(b): TEM image of LM3 catalyst prepared at pH 10

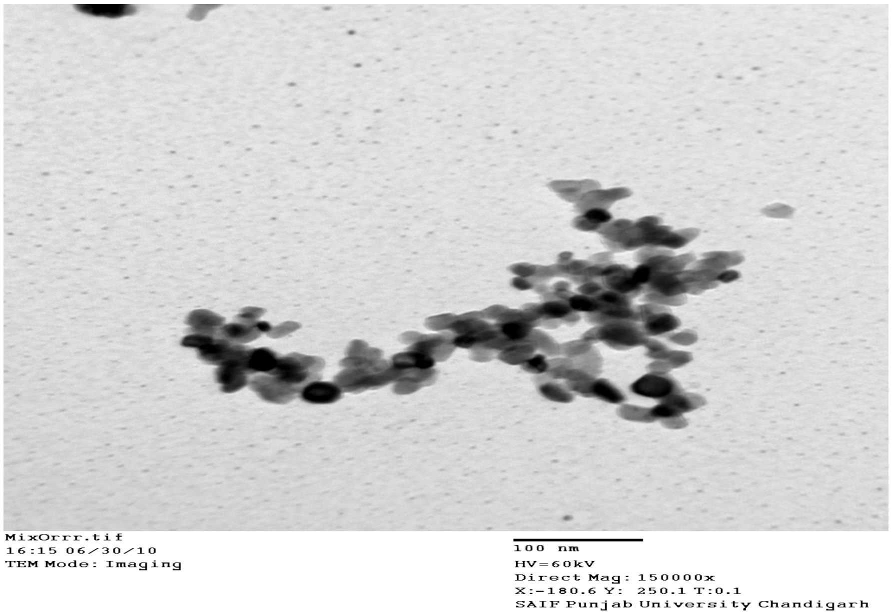


Figure 4.1(c): TEM image of LM3 catalyst prepared at pH 10

4.1.3. Power XRD pattern of prepared catalysts

(i) Powder XRD pattern of LM3 catalysts at different pH

Powder XRD patterns of LM3 catalysts prepared at pH of 10, 9.5, 10.5 and 9.4 are shown as a, b, c and d in figure 4.2. Catalyst prepared at pH 9.4 (fig 4.2d) shows the diffraction lines related to $La_2(CO_3)_2(OH)_2$ (PDF 46 -0368). Catalyst LM3 prepared at pH 9.5 (fig 4.2b) exhibit the pattern similar to $La_2(CO_3)_2(OH)_2$ (PDF 46-0368) and La_2O_3 (PDF 83-1345). Both LM3 prepared at pH 10.5 (fig 4.2c) and prepared at pH 10 (fig 4.4a) shows the diffraction lines related to La_2O_3 (PDF 83-1345), La_2MgO_x (PDF 42-0339), $La_2(CO_3)_2(OH)_2$ (PDF 46 -0368) and MgO (PDF 77-2179). The formation of La_2MgO_x phase implies that formation of a homogeneous solid solution takes place during the preparation of catalyst.

(ii) Powder XRD pattern of La/Ca catalysts

Powder XRD patterns of La/Ca catalysts LC1, LC2, LC3 and LC4 are shown as (a), (b), (c) and (d) respectively in figure 4.3. LC1 catalyst show the diffraction lines related to La_2O_3 (PDF 83-134), $Ca(OH)_2$ (PDF 84-1274). All other catalysts LC2, LC3, LC4 exhibit pattern similar to La_2O_3 (PDF 83-134) and $La(OH)_3$ (PDF 36-1481). There was no phase corresponding to the solid solution of La and Ca.

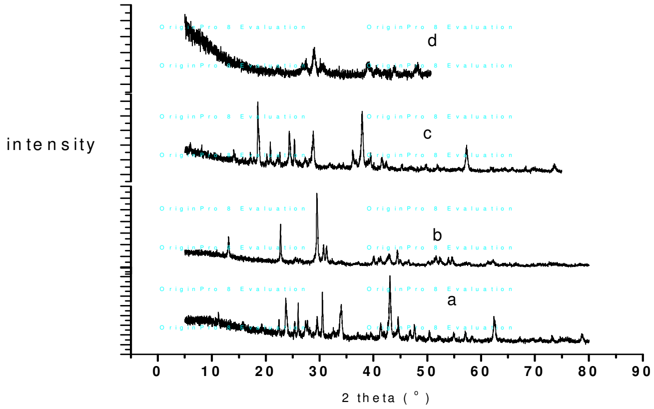


Fig.4.2: Powder XRD pattern of LM3 catalysts prepared at different pH (a) pH 10 (b) pH 9.5 (c) pH 10.5 (d) pH 9.4

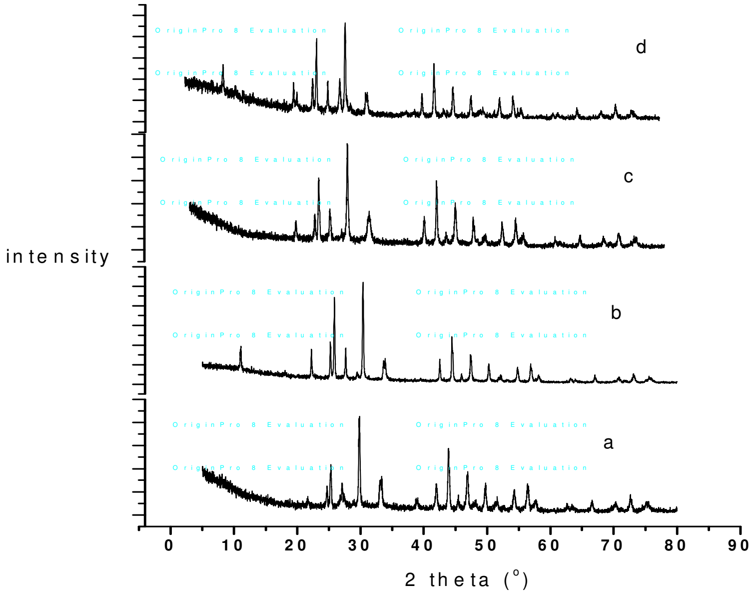


Fig. 4.3 Powder XRD patterns of La/Ca catalyst. (a) LC1 (b) LC2 (c) LC3 and (d) LC4

(iii) Powder XRD pattern of La/Mg/ Ca catalysts

Powder XRD patterns of La: Mg: Ca catalysts LM2C, LM3C, LM4C and LM5C are shown as (a), (b), (c) and (d) respectively in Figure 4.4. The phases corresponding to the La_2O_3 (PDF 83-1345), $La_2(CO_3)_2(OH)_2$ (PDF 46-0368) and La_2MgO_x (PDF 42-0339) are found to be present in LM2C. Powder XRD spectra of LM3C catalyst confirming the presence of MgO (PDF 77-2179) and $La(OH)_2$ (PDF 36-1481). LM4C catalyst exhibit the diffraction pattern similar to La_2O_3 (PDF 83-1345), La_2MgO_x (PDF 42-0339), MgO (PDF 77-2179) and $La(OH)_2$(PDF 36-1481). Presences of La_2MgO_x phase confirm the formation of solid solution during catalyst preparation. LM5C catalyst which has maximum proportion of magnesium shows diffraction lines similar to MgO (PDF 77-2179).

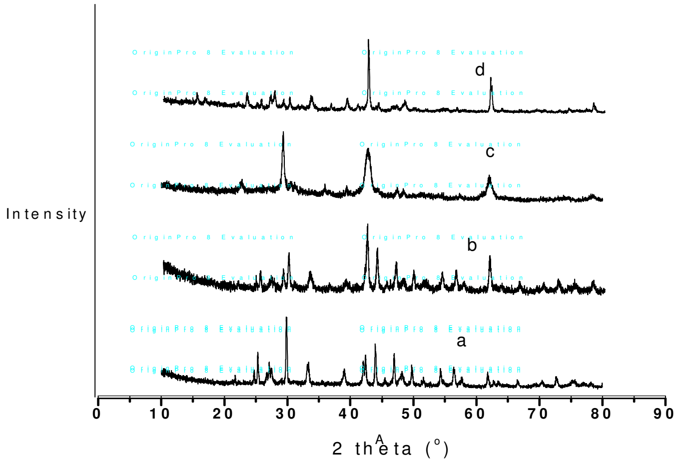


Fig.4.4: Powder XRD patterns of La/Mg/Ca catalyst. (a) LM2C (b) LM3C (c) LM4C (d) LM5C

4.2 Catalytic Activity

4.2.1) LM3 catalysts

In order to observe the catalytic activity of LM1, LM2, LM3 catalysts, a series of reactions were carried out by treating used cotton seed oil (5g) with Methanol (25g) at 65°C in the presence of 200 mg of the catalyst and time taken for complete transesterification is shown in the table 4.2.

Table4.2: Time taken by different La/Mg catalysts

Catalyst	pH for precipitation of catalyst	Time Taken for completion of reaction
LM1	10	9
LM2	10	4.45
LM3	10	4

LM3 catalyst took least time among all La/Mg catalysts for complete transesterification. Further LM3 catalyst was used for optimizing other two parameters viz., effect of catalyst amount and methanol amount.

LM3 prepared at pH 10 was found to be only efficient catalyst for the transesterification. Catalyst LM3 prepared at pH 9.4 and 9.5 was not able to complete the transesterification reaction. Formation of Solid solution as confirmed from the presence of La_2MgO_x phase (Fig. 4.2a) during catalyst preparation at pH 10 might be the reason for good catalytic activity. Smaller particle size of LM3 catalyst prepared at pH 10 as can be seen in Fig.4.1(c) seems to be another reason for good catalytic activity.

Effect of catalyst amount

Transesterification reactions of used cotton seed oil with methanol (1:22 molar ratio) at 65°C were carried out in the presence of varying amount (2-5 wt %) of LM3 as catalyst to determine the optimum amount of catalyst. Effect of Catalyst amount for transesterification is shown in fig 4.5. With decrease in wt% of catalyst from 5 to 2 wt%, the time required for the completion of the reaction increases from 4 h to 6.75 h. Hence 5 wt% of the catalyst was selected for optimizing oil to methanol molar ratio.

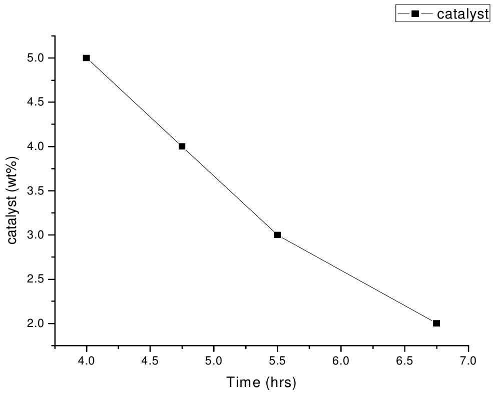


Figure 4.5: Effect of wt% of LM3 catalyst

Effect of methanol amount

Theoretically oil/methanol molar ratio required for the complete conversion of oil to biodiesel is 1:3. But in case of mixed oxide catalyzed transesterification reactions, higher molar ratios of oil: methanol are required for the completion of reaction. To study the effect of oil to methanol molar ratio, a series of transesterification reactions were carried by varying oil to methanol ratio (1:54 to 1:191) with 5 wt% of catalyst at 65°C. As the molar ratio increases from 1:54 to 1:136, the time taken for completion of reaction decreases from 7.75 h to 4h. Further increase in molar ratio does not lead to decrease in reaction time. Hence Molar ratio of 1:136 of oil to methanol was found to be suitable for transesterification reaction.

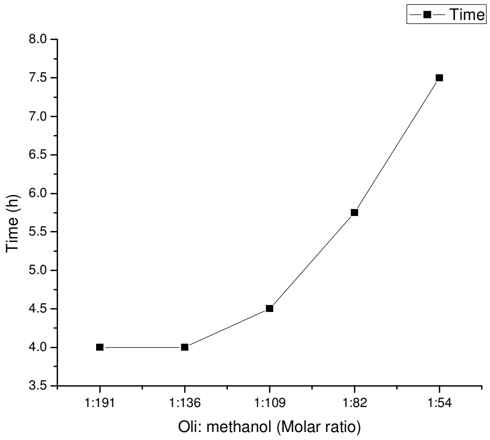


Figure 4.6: Effect of oil:methanol (molar ratio) with LM3 catalyst

4.2.2 La/Ca catalyst

To study the catalytic activity of La/Ca catalysts, a series of reaction were carried out by treating used cotton seed oil (5g) with Methanol (25g) at 65° C in the presence of 200mg of each catalyst (LC1, LC2, LC3, LC4) and the LC2 catalyst showed complete transesterification with in time of 8 h (least time) among the other La/ Ca catalysts. Reaction was not found to complete with LC1 catalyst. Time taken by each La/ Ca catalyst for completing the reaction is given below in the table 4.3. Presence of La $(OH)_3$ phase only in case of LC2, LC3, and LC4 catalysts as can be seen in fig 4.3 may be reason for catalytic activity.

Table 4.3: Time taken by different La/Ca catalysts

Catalyst	pH for precipitation of catalyst	Time Taken for completion of reaction
LC1	10	Not completed
LC2	10	8h
LC3	10	12h 50 min
LC4	10	34h 28min

4.2.3 La/Mg /Ca catalyst

Mixed oxides of La/Ca /Mg with different proportion of Mg viz., LM2C, LM3C, LM4C, and LM5C were used as catalysts (5wt %) for the transesterification of oil (5g) with methanol (25 g) and reaction time of completion is listed in the table 4.4. It was found that LM4C catalyst took lesser time (3 h 40 min) among the La/Ca /Mg catalysts for the completion of reaction. Good catalytic activity of LM4C may be attributed to formation La_2MgO_x phase along with La $(OH)_2$ phase as can be seen in Fig 4.4.

Table 4.4: Time taken by La/Mg/Ca catalyst in different ratio

Catalyst	pH for precipitation of catalyst	Time Taken for completion of reaction
LM2C	10	16 h 15 min
LM3C	10	9h 30 min
LM4C	10	3 h 40 min
LM5C	10	7 h 15 min

Biodiesel Analysis

Analysis of Biodiesel by ^{1}H NMR

Biodiesel prepared from used cotton seed oil was characterized by ^{1}H NMR. The proton NMR spectrum of used cotton seed oil shows a multiplet at 4.1 and 5.2 ppm due to the presence of glyceridic protons along with other hydrocarbon peaks. Appearance of new peak at 3.6 ppm due to the $-OCH_3$ protons and disappearance of glyceridic protons support the formation of biodiesel as shown in figure 4.5(a) and (b).

$$C = \frac{100 \text{ x } (2 \text{ x } I_{M.E})}{3 \text{ x } I_{\text{Methylene proton}}}$$

C = percentage conversion of oil into the corresponding methyl ester.

$I_{M.E}$ = integration value of the protons of the methyl esters

$I_{\text{Methylene protons}}$ = integration value of the methylene protons

The factors 2 and 3 derive from the fact that the methylene carbon possesses two protons and the alcohol (methanol–derived) carbon has three attached protons.

From figure 4.7(b) conversion is about 96%

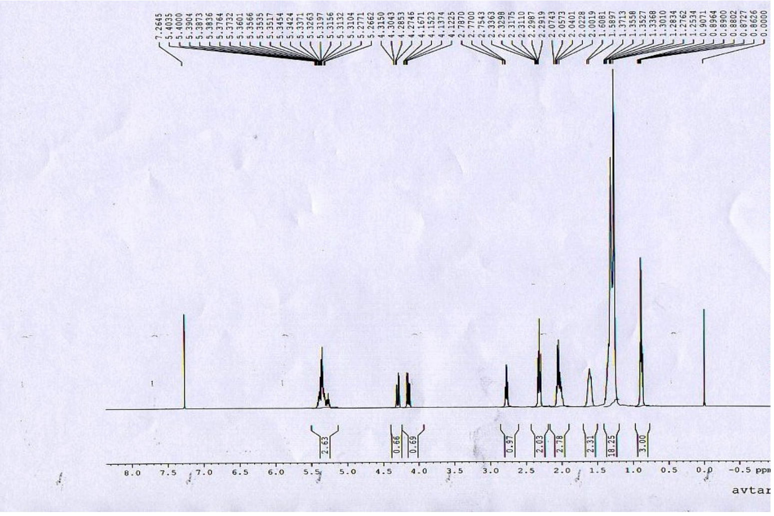


Fig 4.7(a): ^{1}H NMR of used cotton seed oil

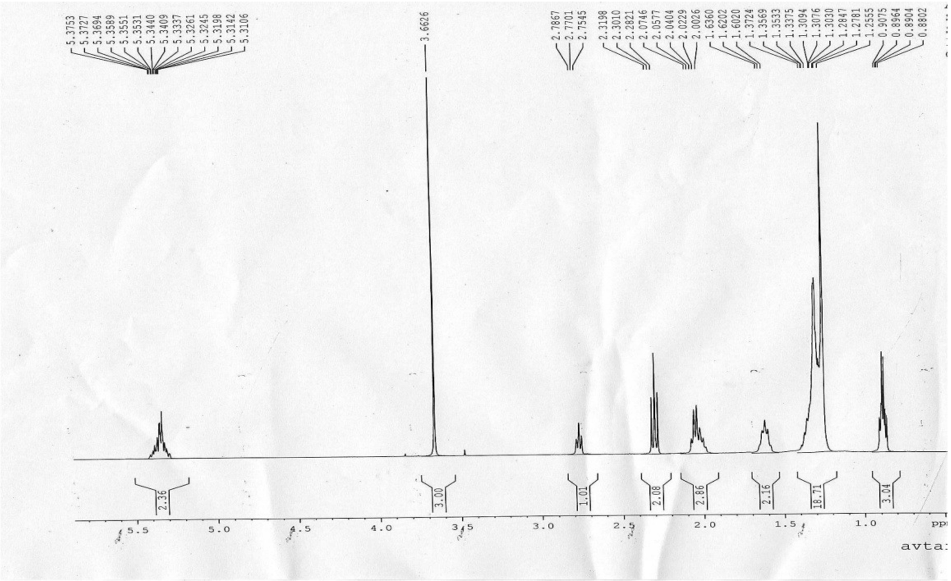


Fig 4.7(b): ^{1}H NMR of biodiesel

Conclusion

La/Mg mixed oxides are efficient catalysts in comparison to La/Mg/Ca and La/Ca oxides. Mixed oxides of La/Mg in1:3 and La/Mg/Ca in 1:4:1 molar ratio prepared at pH 10 are found to be most basic catalysts as according to hammett indicator test and lesser reaction times of completion are observed with these catalysts. Both of these catalysts have phase corresponding to La_2MgO_x i.e. a homogeneous solid solution formed during catalyst preparation which seems to be the reason for higher basic strength and catalytic activity. An amount of 5 wt% of La/Mg catalyst (1:3 ratios) and 1:136 molar ratio of oil to methanol at reflux temperature was worked out to be the optimum reaction parameters for lesser time for completion of reaction. La/Mg/Ca (1:4:1) catalyst completes the reaction within the time period of 3h 45 min when 1: 136 molar ratio of oil: methanol was used with 5 wt% of catalyst at 65^oC. La/Ca mixed oxides (1:1, 1:2, 1:3, and 1:4 wt/wt) were found to be the least active catalysts in comparison to the La/Mg, La/Mg/Ca catalysts.

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