Li-Zr/CaO AS HETEROGENEOUS CATALYST FOR THE TRANSESTERIFICATION OF COTTON SEED OIL

A
Thesis submitted
In the partial fulfilment of the requirement for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

Submitted by:
Shivani Atri
(301402021)

UNDER THE SUPERVISION OF:

Dr. Amjad Ali
Associate Professor
SCBC

Dr. Haripada Bhunia
Professor
Dept. of Chemical Engineering

THAPAR UNIVERSITY
PATIALA
2016

CERTIFICATE

This is to certify that the thesis entitled "**Li-Zr/CaO as heterogeneous catalyst for the transesterification of cotton seed oil**" being submitted in partial fulfilment of requirements for the award of degree of **Master of Science in Chemistry,** submitted in the **School of Chemistry and Biochemistry, Thapar University, Patiala** is a bonafide work carried out under the supervision of **Dr. Amjad Ali,** Associate Professor, School of Chemistry and Biochemistry and **Dr. Haripada Bhunia**, Professor, Department of Chemical Engineering, Thapar University, Patiala and that no part of this project has been submitted for the award of any other degree.

(SHIVANI ATRI)

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

(Dr. AMJAD ALI)
Associate Professor, SCBC,
Thapar University
Patiala, 147004

(Dr. HARIPADA BHUNIA)
Professor,
Department of Chemical Engineering,
Thapar University
Patiala, 147004

Countersigned By:

(Dr. BONAMALI PAL)
Professor and Head, SCBC,
Thapar University,
Patiala, 147004

(Dr. S.S.BHATIA)
Dean, Academic Affairs
Thapar University,
Patiala, 147004

CANDIDATE'S DECLARATION

I hereby declare that the work presented in the thesis entitled, "**Li-Zr/CaO as heterogeneous catalyst for the transesterification of cotton seed oil**" in partial fulfilment of requirements for the award of degree of **Master of Science in Chemistry,** submitted in the **School of Chemistry and Biochemistry, Thapar University, Patiala,** is an authentic record of my own work carried out under the supervision and guidance of **Dr. Amjad Ali**, Associate Professor, School of Chemistry and Biochemistry and **Dr. Haripada Bhunia**, Professor, Department of Chemical Engineering, Thapar University, Patiala and refers other researcher's work which are duly listed in the reference section.

The matter embodied in this thesis has not formed the basis for the award of any other degree of this or any other university.

Date: July 4, 2016

Place: Patiala

(SHIVANI ATRI)

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

(Dr. AMJAD ALI)
Associate Professor, SCBC,
Thapar University,
Patiala.

(Dr. HARIPADA BHUNIA)
Profesor, Dept of Chemical Engineering,
Thapar University,
Patiala

(Dr. BONAMALI PAL)
Professor and Head, SCBC,
Thapar University,
Patiala.

ACKNOWLEDGEMENT

There is always a sense of gratitude which one expresses to others for helpful services they render during all phases of life. First and foremost I would like to thank the almighty for all the countless blessings. And now thanking all those who helped me directly and indirectly in completion of this work.

It is the matter of immense pleasure to acknowledge my debt to my revered teachers and supervisor Dr. Amjad Ali, Associate Professor, School of Chemistry and Biochemistry and Dr. Haripada Bhunia, Professor, Department of Chemical Engineering, Thapar University, Patiala. It is because of their priceless guidance, innovative and constructive ideas for having given me complete independence, affectionate encouragement to put my desire and thought, which paved the way for my successful completion of this work. It is my privilege to work under them.

I am also thankful to all teaching and non-teaching staff members of the department for their invaluable cooperation and help during the entire tenure of my studies in the department.

I take this opportunity to thank all research fellows especially Ms. Avneet Kaur, Ms. KM Abida, Ms. Rashi Malhotra, Ms. Manpreet Kaur, Mr. Siddharth Sharma and Mr. Himmat Jaglan for their constant cooperation and timely help.

Life at Thapar University, Patiala has been enjoyable with friends: Sachin Bishnoi, Pallvi Bhatia and Pallavi Jain. I thank them all for their great company.

In the end, I wish to express my deep sense of gratitude to my family, for supporting and encouraging me at every step of my work. It is the power of their blessings, which has given me the courage, confidence and zeal to work hard.

Date: July, 2016

Regards,

Place: Patiala

(SHIVANI ATRI)

INDEX

ABSTRACT

In present work a series of Li impregnated Zr/CaO has been prepared by varying the Li contents in the range of 1-12 wt%. The prepared catalyst was characterized by powder XRD, Hammett indicator test, SEM and TEM studies. This catalyst was employed for the transesterification of triglycerides to yield fatty acid methyl esters (FAME) and also for carboxylation of glycerol in a high pressure reactor. ^{1}H-NMR technique was employed to quantify the FAME yield obtained during the transesterification reaction. Under the optimized reaction conditions of 5 wt% catalyst (with respect to oil), 65 °C reaction temperature, methanol to oil molar ratio of 12:1, > 98% FAME yield was obtained in 1 h of reaction duration. For carboxylation, pressure of CO_2 was kept at 5 bars and temperature varied from 80 ^{o}C to 100 ^{o}C and conversion of glycerol to glycerol carbonate is still under consideration.

CHAPTER-1

INTRODUCTION

1.1 BIOFUELS

With the increasing concern about global warming and environment pollution, biofuels are gaining a lot of interest and popularity in the field of research. Atmospheric carbon dioxide emitted by cars is a major green house gas causing global warming which further escalates the importance of biofuels. Biofuels is actually a broad term used for any kind of fuel derived from living matter so much so that gasoline and diesel comes under the category of ancient biofuels. The only difference is that new age biofuels are made from plants whereas ancient bio fuels are made from fossils or decomposed plants and animals buried millions of years ago. They are called as fossil fuels. Various kinds of biofuels are used in countries around the world today with major stress given on ethanol fuels.

Various other types of bio fuels are bio-alcohol, biodiesel, green diesel, bio-ethers, biogas, algae-based fuels, bio-hydrogen etc.

1.1.2 Biodiesel

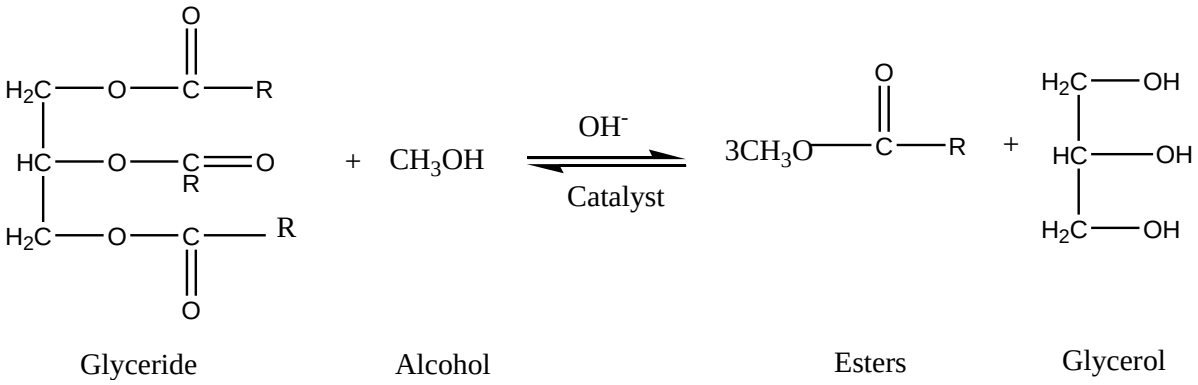
Biodiesel, chemically known as fatty acid alkyl esters, is a renewable and ecofriendly substitute for conventional diesel fuel. Many countries all over the world are using edible fatty oils such as rapeseed, palm, soybean, sunflower, linseed, coconut etc. as a raw material for biodiesel. In addition to edible oils, non-edible oils such as tallow, lard or used frying grease and oil have not been reported well for the production of biodiesel. Other non-edible tree-based oil has great potential of being transesterified for making biodiesel.

However, a major obstacle in the commercialization of biodiesel production from edible vegetable oils is their high production cost, which is due to the demand for human consumption. Reducing the cost of the feedstock is necessary for biodiesel's long term commercial viability. One way to reduce the cost of this fuel is to use less expensive feedstocks including waste cooking oils and vegetable oils that are non-edible and/or require low harvesting costs (Deng *et al*., 2012). Used cooking oils as raw material for biodiesel is in high demand because it lowers the cost of production of biodiesel and also favours the most commonly used process of production i.e. transesterification of animal fats and oils. The FFA content is higher in edible oil which leads to saponification of the product (Su and Guo, 2014) High quality glycerol obtained as by product are also one of the factors favouring the

process used. Other processes used and known for the production of biodiesel are thermal cracking which is also known as pyrolysis; microemulsions and direct use and blending.

1.2 TRANSESTERIFICATION

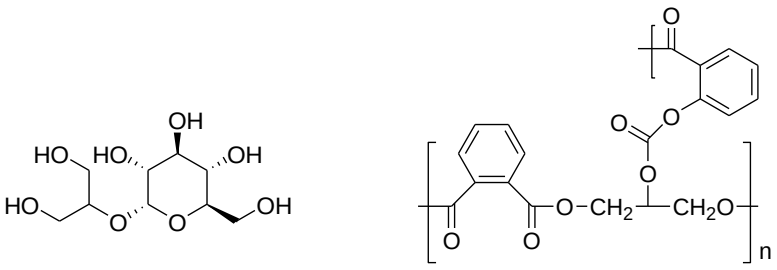
In organic chemistry, the process of another alcohol exchanging the alkoxy group of an ester compound is called transesterification. These reactions are often catalyzed by the addition of an acid or base. Transesterification is the commonly used process to produce biodiesel as shown in Scheme 1. In this process glycerol is obtained as a side-product. The process of transesterification is affected by the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature and purity of reactants. We can monitor transesterification reactions by various techniques like TLC, GC, HPLC, GPC, ^{1}H NMR and NIR. (Meher *et al*., 2006)



Scheme 1: Transesterification of the vegetable oil

1.3 GLYCEROL

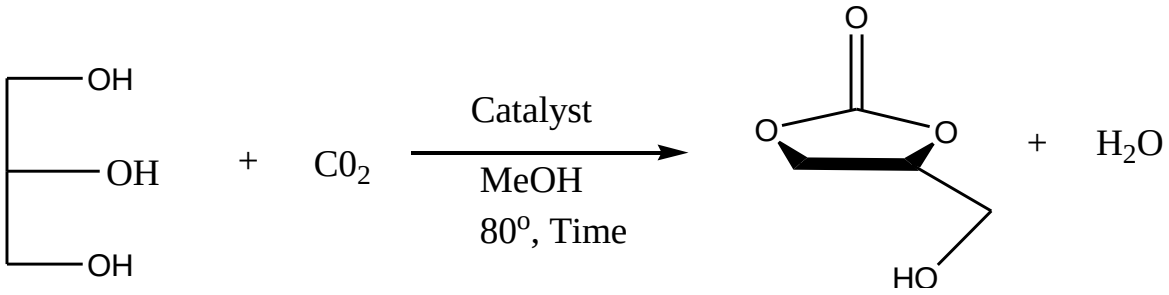
Glycerol produced as a by-product during biodiesel production is in surplus quantity i.e. 8–10% by weight (Yoo *et al*., 2001). This means for every 3 mole of triglyceride, 1 mole of glycerol is produced. The ongoing research and remarkable growth in the field of biodiesel is leading to overproduction and therefore oversupply of glycerol. There is now becoming a need to reduce this over supply and production of glycerol as with this trend, it is foreseen that glycerol production may increase to 4 megatons by 2020(Meghan *et al.*, 2015). Glycerol is also hygroscopic in nature. Some of the commercially available glycerol derivatives are shown in Fig. 1.



2-*O*-(α-D-glucopyranosyl)-*sn*-glycerol ; Glyptal

Fig. 1: Structure of various glycerol derivatives.

Glycerol carbonate is one of the most important products that glycerol can be yielded into and it can also be considered as a renewable product. It has diverse applications in various fields such as polymer materials or in synthetic organic chemistry. Glycerol carbonate is commonly produced by indirect method of reacting glycerol with carbonyl sources such as dialkyl carbonate, phosgene, urea etc (Yoo *et al*., 2001; Rokicki *et al*., 2005; Claude *et al*., 1996; Vieville *et al*., 1998). Carbon dioxide is used for the direct carbonation of glycerol and it would be one of the most important research opportunities since two resources available in abundance could give a valuable product with 87% atom efficiency making the process one of its best(Clark *et al.*, 2006).



Glycerol Glycerol Carbonate

Scheme 2: Carboxylation of Glycerol into Glycerol Carbonate

1.4 LITERATURE REVIEW

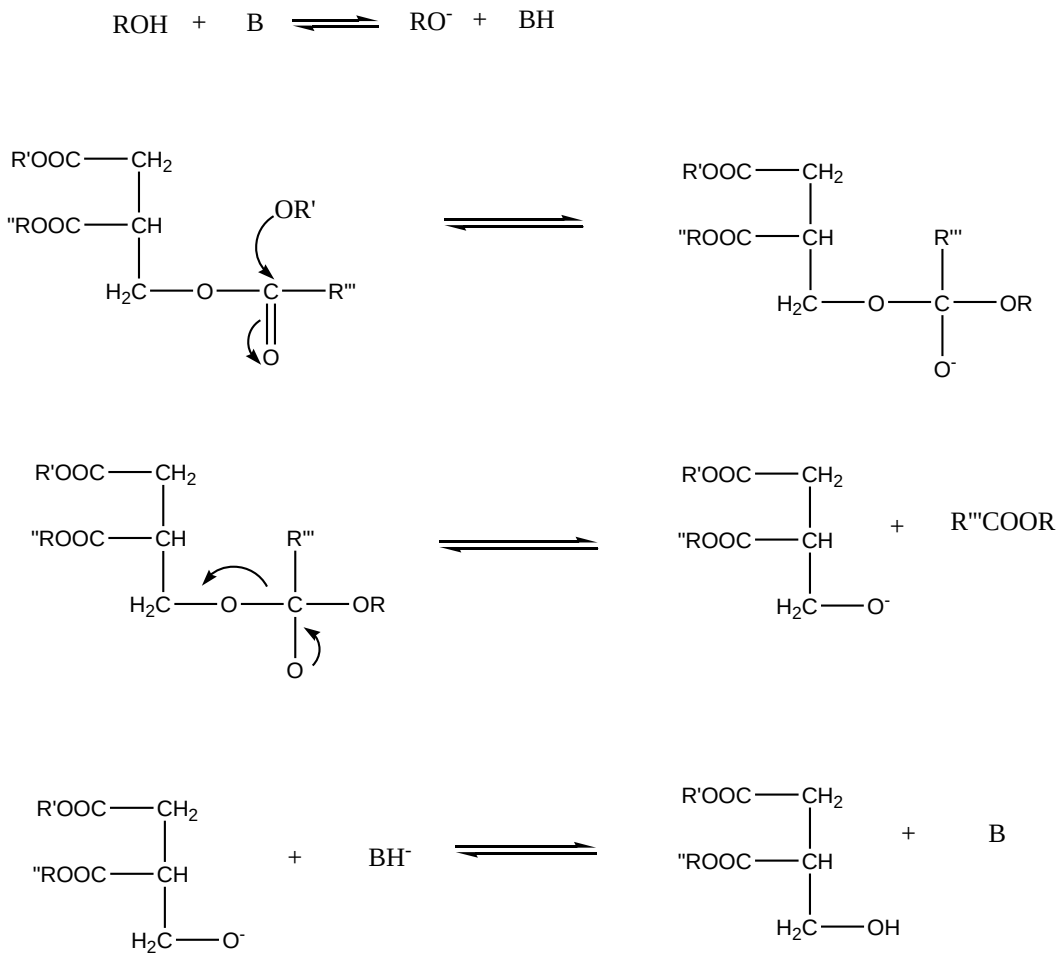
There are two ways of carrying out the process of transesterification: by taking the catalytic approach or the non-catalytic approach. In the non-catalytic process, conditions employed are supercritical since very high temperature and pressure is used (Coniglio *et al*., 2014). The catalytic approach can be further broken down into biocatalysts or chemical catalysts. The bio-catalysts include various enzymes such as lipase that can carry out the production of bio-diesel (Vasile *et al*., 2012). Chemical catalysts employed can be acidic or alkaline. It can also be heterogeneous or homogeneous. Irrespective of the nature each catalyst has its own advantages and disadvantages based on the compounds like FFA and water which are undesirable. Many other factors like temperature, moisture content, type of alcohol used etc. affects the activity of the catalyst.

On the similar lines of it, although different types of alcohol like methanol, ethanol and so on can be used, the most important and most frequently used is methanol. Methanol has many advantages over the rest of its counterparts because of its low cost and chemical and physical advantages such as shortest alcohol chain and polar nature.

1.5 HOMOGENEOUS CATALYSTS

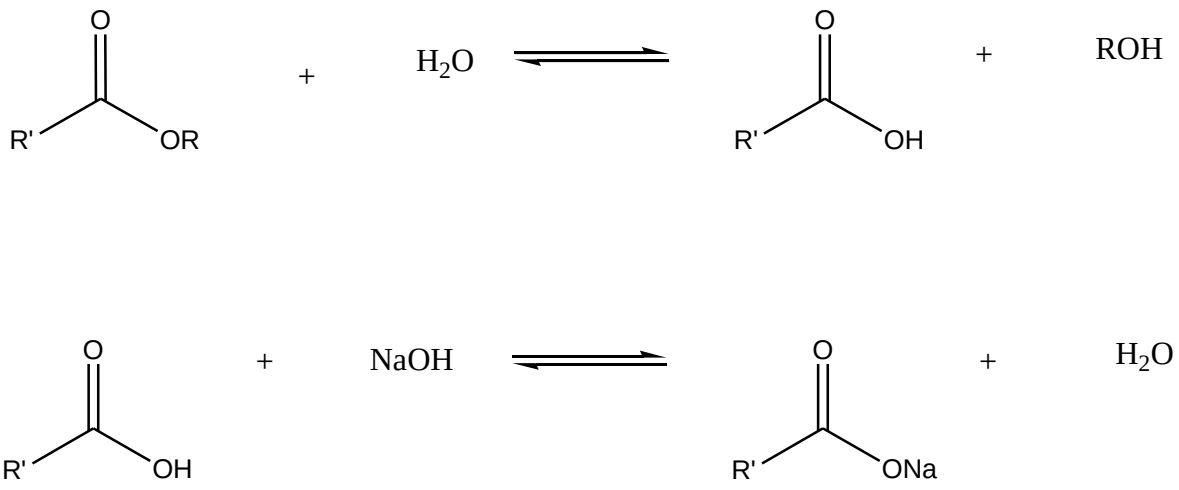
1.5.1 Alkali-catalysts

Homogeneous Alkali-catalysts like NaOH, KOH, CH_3ONa have been used by various researchers since they are cost-efficient and are very readily available (Fukuda *et al*., 2001). They are active even under ambient conditions and act as good catalysts for the production of biodiesel. When the catalytic activity of NaOH and KOH were compared, it was found out that KOH reacted faster. However, NaOH is the best catalyst for waste cooking oil has been concluded by majority of researchers (Doroda *et al*., 2004).



Scheme 3: Base catalyzed transesterification reaction mechanism

The process of transesterification using alkali catalysts as shown in Scheme 3 has some drawbacks i.e. energy consumed is very high and so the overall capital equipment cost increases and other safety issues also comes into play. On top of it all, these alkali catalysts are moisture sensitive and also reactive to the FFA (Free Fatty Acid) content in the feedstock. Presence of moisture in sufficient amounts can yield to saponification (as shown in Scheme 4) and therefore decreases the yield of ester (Canakci *et al*., 1999) Saponification also makes the separation of glycerol difficult from the ester yield (Freedman *et al*., 1984). It increases the viscosity and forms an emulsion which further adds to the problem.

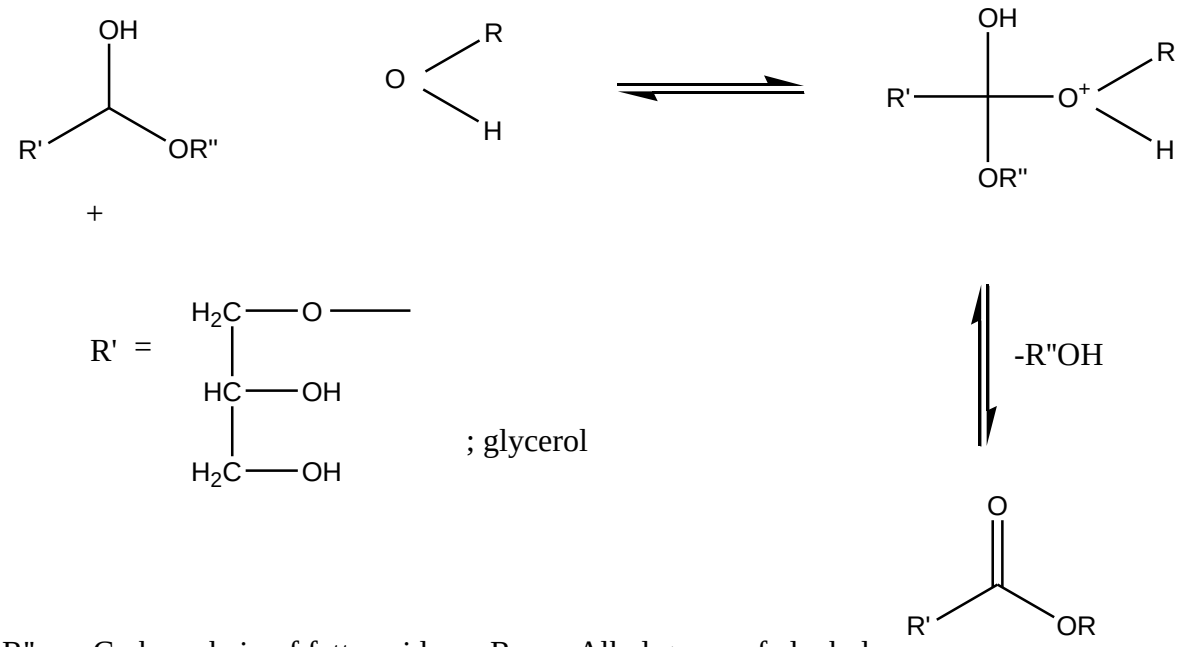


R' = Carbon chain of fatty acid ，R = Alkyl group of alcohol

Scheme 4: Saponification of fatty acids in the presence of base.

1.5.2 Acid-catalysts

Other homogeneous catalysts can also be used which comes under the category of homogeneous acid catalysts. These catalysts like sulphuric acid, hydrochloric acid (Wang *et al*., 2006), phosphoric acid, sulfonated acid overcomes many of the drawbacks of alkali based catalysts. They have better results with FFA greater than 1% for vegetable oil and they are also insensitive to free fatty acids. The mechanism is shown in Scheme 5. During the reaction, the acid is directly mixed with oil and both the esterification and transesterification reaction takes place simultaneously thereby decreasing the production cost by processing low-quality and cost feedstocks high in FFA (Kulkarni *et al*., 2006). It is a single step reaction because acids have esterification reagents and in this single step they play the role of a solvent (Cervero *et al*., 2008). The reaction however is slow and hence the reaction time is increased. They are not as effective as alkali catalysts since they require harsh and sometimes incompatible conditions such as very high temperature, longer time period and high methanol to oil molar ratio.



R" = Carbon chain of fatty acids , R = Alkyl group of alcohol

Scheme 5: Acid-catalyzed transesterification reaction mechanism

Another prominent reason which does not support the use of acid catalysts is the production of water as a by-product which leads to the deactivation of the catalyst. When the reactivity is compared, acid catalysts show less reactivity as compared to alkali catalysts. Moreover, acids can produce a large number of salt-interaction which corrodes the reactor and hence a special costlier acid reaction vessel is used.

After completion of the reaction, both homogenous acid and base catalysts must be neutralised and removed from the products through washing it with water which generates huge amounts of industrial effluents.

1.5.3 Acid and alkali catalyzed two-step transesterification

The biggest problem encountered by the researchers in the above two processes were longer reaction duration and saponification. The solution many researchers derived for this problem was two-step acid and alkali catalyzed transesterification to limit the problems.

In the first step, FFA was esterified using acid catalysts to decrease their levels to lower than 1% and then in the second step, WCO was transesterified using alkali catalysts. The results found proved that two step was indeed a better way than the single step reaction. The advantages included high efficiency, decreased reaction time, lower energy consumption low equipment cost, no acidic waste treatment. In addition, (Encinar *et al*., 2007) concluded that two-step reaction has higher conversion of up to 30% in comparison with single-step process.

However, the most challenging part in this reaction is the catalyst removal in both stages. The only challenge all the above homogenous catalysts put up is the removal of catalyst once the process has ended. Removal and recovery of catalyst makes the job tedious.

1.6 HETROGENOUS CATALYSTS

Although the production cost of biodiesel is high when compared with the petroleum based diesel fuel, its eco-friendly nature wins over, but we still need to control the production costs to make it more pocket-friendly. There are two main factors that contribute to the cost of biodiesel: the cost of processing and the cost of raw materials. To keep them in control, heterogeneous catalysts can provide an attractive solution. Since these catalysts can be separated easily, it can be recovered and hence reused. These catalysts also doesn't produce contaminated product and hence washing of product to get the ester is not needed. This helps controlling both the factors. Hence introducing a solid catalyst in industrial production could reduce its price and make it more viable to the public competing neck to neck with petroleum based diesel.

We can classify heterogeneous acid and basic catalysts as Brönsted or Lewis catalysts, although sometimes both types of active sites are present in one catalyst. A detailed description of some reaction mechanisms can be found in the paper of (Lotero *et al*., 2006). Various types of heterogeneous catalysts such as alkaline earth metal oxides and derivatives (Yoo *et al*., 2010), alkali metal oxides and derivatives(Arzamendi *et al*., 2007), ion exchange resins(Marchetti *et al*., 2008), sulphated oxides (Alba-rubio *et al*., 2010), boron group base heterogeneous catalyst(Jaya, 2011), heterogeneous transition metal oxides and derivatives(Antunes *et al*., 2008), mixed metal oxides and derivatives(Xu *et al*., 2008), carbon based heterogeneous catalysts (Shu *et al*., 2010), waste material based heterogeneous catalyst(Deka *et al*., 2011) and enzyme based heterogeneous catalyst(Hama *et al*., 2004), have been used in various biodiesel production. These heterogeneous catalysts can be prepared by a variety of methods like physical mixing, impregnation, calcinations, precipitation and hydrothermal synthesis. Combination of these techniques is also used so as to get the highest catalytic activity.

1.6.1 Acid-catalysed

Acidic solid catalysts can carry out esterification as well as transesterification of waste cooking oil which makes it highly useful and cost-efficient. Being heterogeneous, it can be

easily separated which further adds to its advantages. Other advantages include its insensitive nature to FFA content, no water washing needed for product, low amount of catalyst required, eco-friendly, higher yield of product obtained, does not corrode the container. (Jacobson *et al*., 2008) researched for a dynamic solid acid catalyst for simultaneous esterification and transesterification reactions and he found out that among (MoO_3/ZrO_2, MoO_3/SiO_2, WO_3/SiO_2, WO_3/ SiO_2-Al_2O_3, and ZS/Si) the zinc stearate (ZS) impregnated on silica gel (ZS/Si) gave a good 98% conversion making it best out of all of them.

But the few drawbacks encountered are: at low temperature, solid acid catalysts show low activity and only after the reaction temperature is increased to 170°C and more, we get a good reaction rate. Also the range of strength for very strong Lewis acidic catalysts is less in transesterification reactions.

1.6.2 Base-catalysed

It has been found that supported base catalysts are leading best catalysts for biodiesel production. Different types of catalysts that's been researched includes Calcium Oxide[49], modified CaO by trimethlychlorosilane(TMCS)(Tang *et al*., 2011), nano-magnetic KF/CaO-Fe_3O_4(Hu *et al*., 2011), and other solid base catalyst which are supported such as EU_2O_3/Al_2O_3(Li *et al*., 2007), Na/NaOH/y-Al_2O_3(Kim *et al*., 2004). These catalysts have reported high yield and are inexpensive. Several other catalysts like potassium (Xie *et al*., 2006) impregnated on alumina and calcined at a temperature of 500-600°C showed good activity and reported a good yield. K_2CO_3 loaded on MgO and Al_2O_3 also gave a good yield in rapeseed oil transesterification using methanol at 60-63°C.

(Shumaker *et al*., 2007) studied and explained the transesterification of soybean oil by using a calcined Li/Al layered double hydroxide catalyst. The reaction time reported was low (~2 h) and the catalyst loadings required were also low (2-3 wt%) . The yield found out was high. Other heterogeneous catalysts are reported in Table 1.

Table 1: Different heterogeneous catalysts used in transesterification reaction.

Catalyst	Vegetable oil	Reaction temp (^oC)	Methanol.: Oil Ratio	Catalyst amount (wt %)	Reaction time(h)	FAME yield (%)	Ref
MgO, MgO/Al_2O_3	soybean	180	12:1	5	1	92	Bournay *et al*., 2005
KOH/sodium zeolite	soybean	65	10:1	3	8	85	Kouzu *et al*., 2012
Basic ETS 10	soybean	100	6:1	10	3	92	Kouzu *et al*., 2012
KF/ZnO	soybean	65	10:1	5	9	87	Dekhordi *et al*., 2012
PbO	soybean	215	7:1	-	2	89	Ochoa *et al*., 2009
La/Zeolite	soybean	160	14.5:1	-	4	48.9	Ochoa *et al*., 2012
$CaTiO_3$, $CaMnO_3$	rapeseed	60	6:1	-	10	90	Aresta *et al*., 2006
Zr/CaO	Jatropha	65	15:1	5	-	99	Georgea *et al*., 2009
Li/CaO	cottonseed	65	12:1	5	2.5	98	Aresta *et al*., 2008
Zn/CaO	vegetable	65	9:1	5	0.75	99	Dibendetto *et al*., 2011

Industrially (Bournay *et al*., 2005) used zinc and aluminium (Zn-Al) mixed-oxide and explained its reaction process. He reported high yields of biodiesel produced by performing the reaction at higher temperature. The comparison of CaO and Zn-Al is described in Table 2.

Table 2: Comparison of catalysts used industrially as reported

Catalyst	Temperature	Pressure	Time	Yield	Reference
Zn-Al	483-523 K	3-5 MPa	-	High	Bournay *et al.*, 2005
CaO	333 K	Atmospheric	2 h	97%	Kouzu and Hidaka, 2012

Also the yield of Biodiesel increased by increasing the temperature and by increasing the oil/methanol ratio while using CaO. Therefore researchers concluded that CaO was a very feasible catalyst and can be used in the industrial production of biodiesel. The only drawback was CaO catalyst leeching. Although this can be overcome by polishing the biodiesel, a modified CaO catalyst is needed.

(Dehkordi and Ghasemi *et al*., 2012) prepared $CaO\text{-}ZrO_2$ mixed oxide as stable catalyst Although when the ratio of Ca to Zr was increased, catalytic activity also showed an increase, the problem of leeching was still not solved.

1.7 CATALYSTS USED FOR CONVERSION OF GLYCEROL INTO GLYCEROL CARBONATE

Glycerol can be yielded into Glycerol Carbonate which is a renewable product. Various processes can be employed namely glycerolysis, transesterification, phosphogenation, and carboxylation (see Fig. 2).

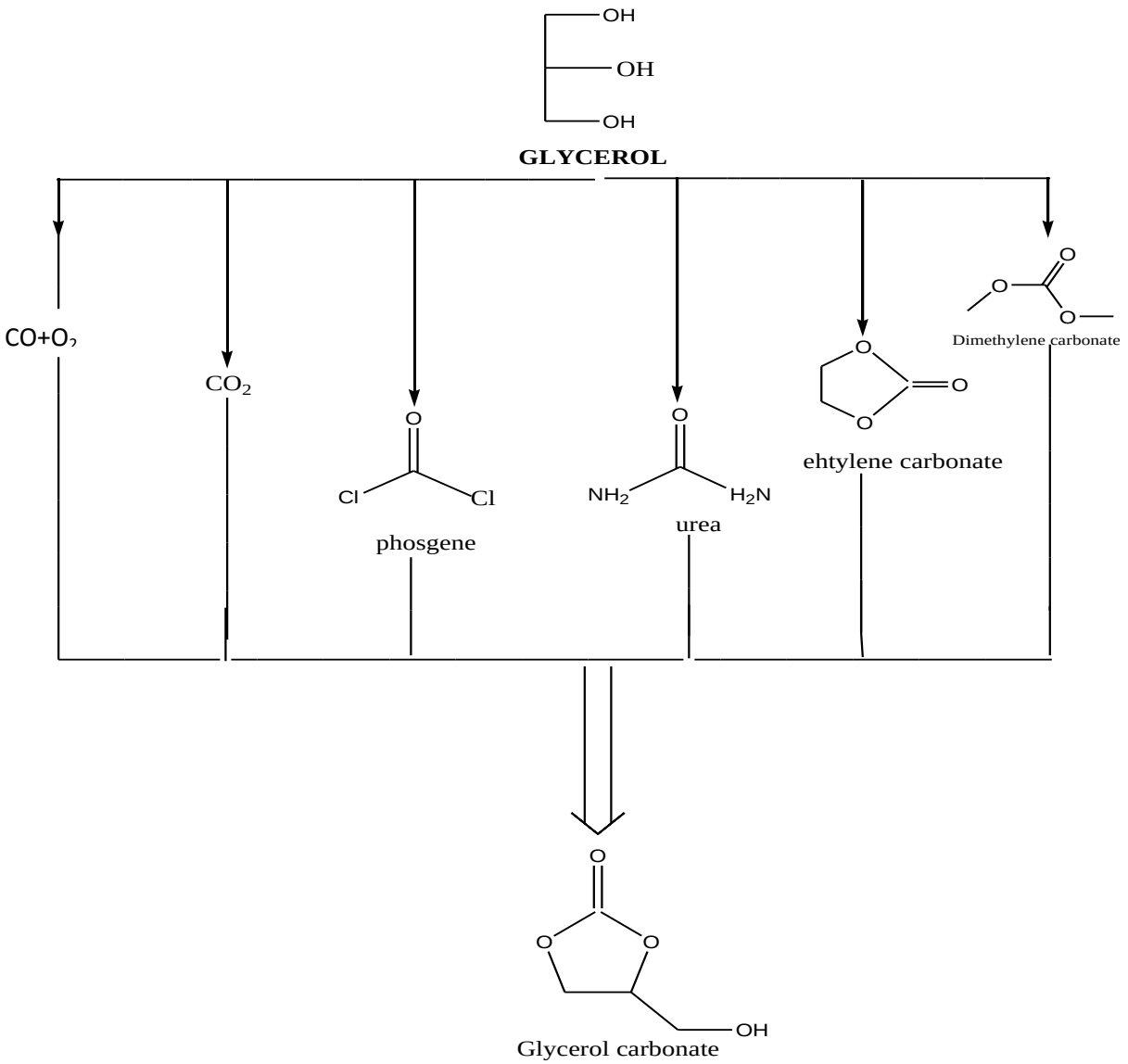


Fig. 2: Various routes of Glycerol Carbonate synthesis

1.7.1 Transesterification

(Ochoa-Gomez *et al*., 2009) reported several homogenous alkali catalysts for e.g. K_2CO_3, KOH, NaOH has shown high conversion under mild conditions but the task of separation and further catalyst neutralisation is a problem and a drawback to the use of these catalysts.

Triethylamine used as homogeneous catalyst gives very high selectivity (91%) and glycerol conversion (99%) at reaction temperature of 68-88°C (Ochoa Gomez *et al*., 2012). Among the products, glycerol dicarbonate also formed which proved to be a problem. Other catalysts for transesterification are discussed in the following Table 3.

Table 3: Catalysts that have been researched and then further used in the transesterification reactions.

Catalyst	Reaction conditions	DMC: GLY Ratio	GLY conversion (%)	GLY (% select-ivity)	Reusa-bility cycles	Ref
KNO_3/CaO	70°C,2h,6 wt%	3:1	99.23	85.85	5	Hu *et al*,2015
$NaOH/Al_2O_3$	78°C,1h,3 wt %	2:1	97.9	99	4	Bui *et al*,2013
KOH	80°C,90min,1 wt %	2.5:1	98.7	98.3	-	Du *et al*,2012
CeO_2	150°C,4h,0.5 wt %	6:1	3.5	100	-	Singh *et al*,2014
CaO	75°C,30min,3 wt %	2:1	94.3	94.7	-	Simanjuntak *at al*,2011
K_2CO_3/MgO	80°C,2h,1 wt %	2.5:1	99	98.6	5	Du *et al*,2012
MgO	150°C,4h,0.5 wt %	6:1	96.62	96	-	Singh *et al*,2014
Zn_4La_1	150°C,2h,0.5 wt %	6:1	98.5	97.2	4	Singh *et al*,2014

The process of glycerolysis produces ammonia as a by-product in large quantities which limits its implication in industries. Phosphogenation route is also avoided because of the use of phosgene gas which is toxic in nature. It's handling and processing also creates a lot of problems.

1.7.2 Carboxylation

The utilization of CO_2 is more attractive rather than storage, if economical processes are available. Various catalysts employed for the process of carboxylation of glycerol into glycerol carbonate are discussed in Table 4 and 5.

Table 4: Catalysts used in the carboxylation reaction of glycerol

Catalyst	Reaction conditions	Pressure CO_2	Glycerol conversion (isolated)	References
n-$Bu_2Sn(OMe_2)$	15h,453K,6 wt %	5 MPa	6.86 %	Dibenedetto *et al.*, 2006
$Sn(OMe_2)$	5h,373k,1 mol %	5 MPa	-	Dibenedetto *et al.*, 2006
$Bu_2(SnO)$	6h,453K,6 wt %	5 MPa	2.30 %	Munshi *et al*., 2009
Al_2O_3/CeO_2	15h,453K,0.3 %	5 MPa	32 %	Aresta *et al,* 2008.
Nb_2O_5/CeO_2	15h,453K,0.3 %	5 MPa	-	Dibenedetto *et al.*, 2006

Table 5: Comparison of catalysts used in the carboxylation process of Glycerol

Reactants	Catalyst	Conditions	Product
Stochiometric amounts of glycerol, urea and Co_2.	2.7 % weight of catalyst	Temp -140^0 C Pressure – 40 mbar of CO_2	Glycerol Carbonate
Catalyst used		**Observations**	
Zn-salts		Highest yield of Glycerol Carbonate. ($ZnCl_2$- 75.1 %, $Zn(NO_3)_2$-63.4 %)	
$MgCl_2$		Good results.	
$CaCl_2.2H_2O$		End mixture got thickened up in honey like matter.	

Wt % and mol % are used for the concentration of catalyst and the solvent used is TEGDME.

- Catalysts like $ZnCl_2$, $MgCl_2$, Zn $(NO_3)_2.6H_2O$, alumina and H-ZSM-5 were tested in amount of 2.7 wt % of glycerol. $CaCl_2$. $2H_2O$ was used in amount of 9.1 wt %.

When $ZnCl_2$ was calcined, it led to the formation of particles of low solubility and the catalyst melted. Without modification, it formed soluble solutions and homogeneous reaction mixtures. Other catalysts like Al/Ce mixed oxides (10, 20 and 40%); 1% Fe/Ce mixed oxides; Fe/Ce mixed oxides (3 and 7%) were also synthesised.

Both the processes of transesterification of vegetable oil and conversion of glycerol into glycerol carbonate are important and should be made more cost-efficient. One way to do so is to use the same catalyst for both the processes. And therefore following objectives were identified for this project.

1.8 OBJECTIVES :

- To prepare a heterogeneous mixed metal oxide catalyst for the process of transesterification of triglyceride and for converting glycerol into glycerol carbonate.
- To characterize the catalyst by SEM, XRD, NMR and Hammett Indicator test.
- To test the catalyst by varying the parameters and report the efficiency.

CHAPTER- 2

EXPERIMENTAL METHODS

2.1 MATERIALS

Cotton seed oil (C.O.) purchased from the nearby local shops in Patiala. $ZrOCl_2 .8H_2O$, CaO, $LiNO_3$, methanol, hexane, ethyl acetate (AR grade), glycerol, glycerol carbonate, Dimethyl carbonate(DMC), Tetra ethylene glycol dimethyl ether (TEGDME) were purchased from Spectro-chem and were used as it is without any further processing. Silica gel for Thin Layer Chromatography (TLC) and silica doped on aluminium plates were purchased from Loba Chemie, India.

2.2 METHODS

Powder X–ray diffraction (XRD) patterns were recorded on a PANalytical's X'Pert Pro using 0monochromatic Cu Kα radiation (λ=1.54060 Å) by scanning the samples over a 2θ range of 5–80°.

Field emission scanning electron microscopy coupled with energy dispersive X–ray spectrometry (FESEM–EDX) was performed on JEOL JSM 6510LV. Fourier transform–nuclear magnetic resonance (FT–NMR) spectra of FAAE and vegetable oils were recorded on a Bruker Avance–II (400 MHz) spectrophotometer. Transmission electron microscopy images of the sample were recorded on Tecnai G2 20 instrument. For sample preparation, powdered sample was mixed with ethanol and ultrasonicated for 1 h to suspend the particles in solvent. A small drop of this suspension was placed on a copper grid and solvent was dried prior to the analysis.

The basic strength of the catalysts (pK_{BH+}) was obtained by using Hammett indicators. Approximately 100 mg of the catalyst was shaken in 5 ml of indicators prepared in 0.02 M of methanolic solution. Neutral red (pK_{BH+}=6.8), bromthymol blue (pK_{BH+} =7.2), phenolphthalein (pK_{BH+}=9.3), Nile blue (pK_{BH+}=10.1), tropaeolin-O (pK_{BH+} =11.1), 2,4-dinitroaniline (pK_{BH+}15.0) and 4-nitroaniline (pK_{BH+} =18.4).

The process of carboxylation was done in High pressure reactor (Amar Equipments Pvt. Ltd.) with the autoclave capacity of 400 ml. The design pressure is 100 bars and maximum working temperature is 250 °C.

2.3 CATALYST PREPARATION

Mixed oxide Zr/CaO catalyst was prepared by simple wet impregnation method. In this method 3 gm of CaO was taken in 30 ml of deionised water. To it, 1.05 gm of $ZrOCl_2 .8H_2O$

(0.33 M) in 10 ml of water was added drop wise over a period of an hour and the resulted suspension was allowed to stir magnetically for another 3-4 hours. After the stipulated time, suspension was dried in oven at 120 °C to isolate the dry powder of Zr/CaO.

The Zr/CaO was used as a support material for Li ion impregnation. In a typical experiment, 2 g of Zr/CaO was suspended in 30 mL water and to this 10 mL 2M solution of $LiNO_3$ was added drop wise with continuous stirring. Resulted suspension was dried in oven at 120 °C for 12 h and finally calcined at 700 °C for 3 h. Similarly, a series of catalysts were prepared by varying the concentration of Li^+ in the range of 1-12 wt% and labelled as x-Li-Zr/CaO-700, where x is the Li^+ wt% in catalyst.

2.4 TRANSESTERIFICATION OF COTTON SEED OIL

Transesterification reactions were performed in a two neck, 50 mL round bottom (RB) flask equipped with a magnetic stirrer, oil bath and water cooled condenser. RB flask was charged with 5g oil, 2.8 mL of methanol and 0.25 gm of catalyst and reaction mixture was magnetically stirred for 2 h at a temperature of 65 °C. To monitor the progress of the reaction, in every 15 minutes sample from the reaction mixture was withdrawn with the help of a glass dropper. The sample was diluted with hexane and subjected to TLC analysis employing hexane: ethyl acetate (90:10, v/v) as mobile and silica gel on glass plate as stationary phase. TLC was developed in iodine chamber and products were identified on the basis of their retention factor (R_f value) as shown in Fig. 3. The fatty acid methyl esters (FAMEs) produced during the reaction was quantified by proton NMR study following the literature reported procedure (Monteiro *et al*., 2008). The FAME yield was calculated by substituting the appropriate values in equation 1.

$$\text{Percentage FAME yield (\%)} = \{2I_{(methoxy)}/3I_{(methylene)}\} \times 100 \quad (1)$$

Where $I_{(methoxy)}$ and $I_{(methylene)}$ are the area of methoxy (3.6 ppm) and methylene (2.33 ppm) protons respectively in 1H-NMR spectra of FAMEs. An error of ±2% was observed when the FAME yield was quantified by this method.

Fig.3: TLC analysis of (a) cotton seed oil (R_f = 0.63), (b) cotton seed oil derived FAME (R_f = 0.9), (c) methyl oleate standard (R_f = 0.9).

2.5 CARBOXYLATION OF GLYCEROL

The reaction was done in the high pressure autoclave reactor (Fig. 4 and 5) connected with the fittings of the CO_2 cylinder. 75 ml of Tetra ethylene glycol dimethyl ether and 25 ml of glycerol and 2 gms of catalyst was added in the autoclave of capacity 400 ml. The reactor mixture was stirred and heated at a temperature of 80^o C and the reaction was carried out for the time duration of 2-4 hours. The pressure of CO_2 maintained was 5 bars. The reactor was allowed to cool down and then sampling was done. Strip of Silica coated on aluminium plate was cut and standards were marked. All the standards were formed in ethyl acetate i.e. of glycerol; TEGDME; reaction mixture; glycerol carbonate. As shown in Fig. 6, stationary phase taken to develop TLC was silica gel and after TLC was run, the plate was dipped in $KMNO_4$ solution and charred using a hot air gun. TLC of reaction mixture didn't show any spot corresponding to glycerol carbonate, hence formation of glycerol carbonate could be ruled out.

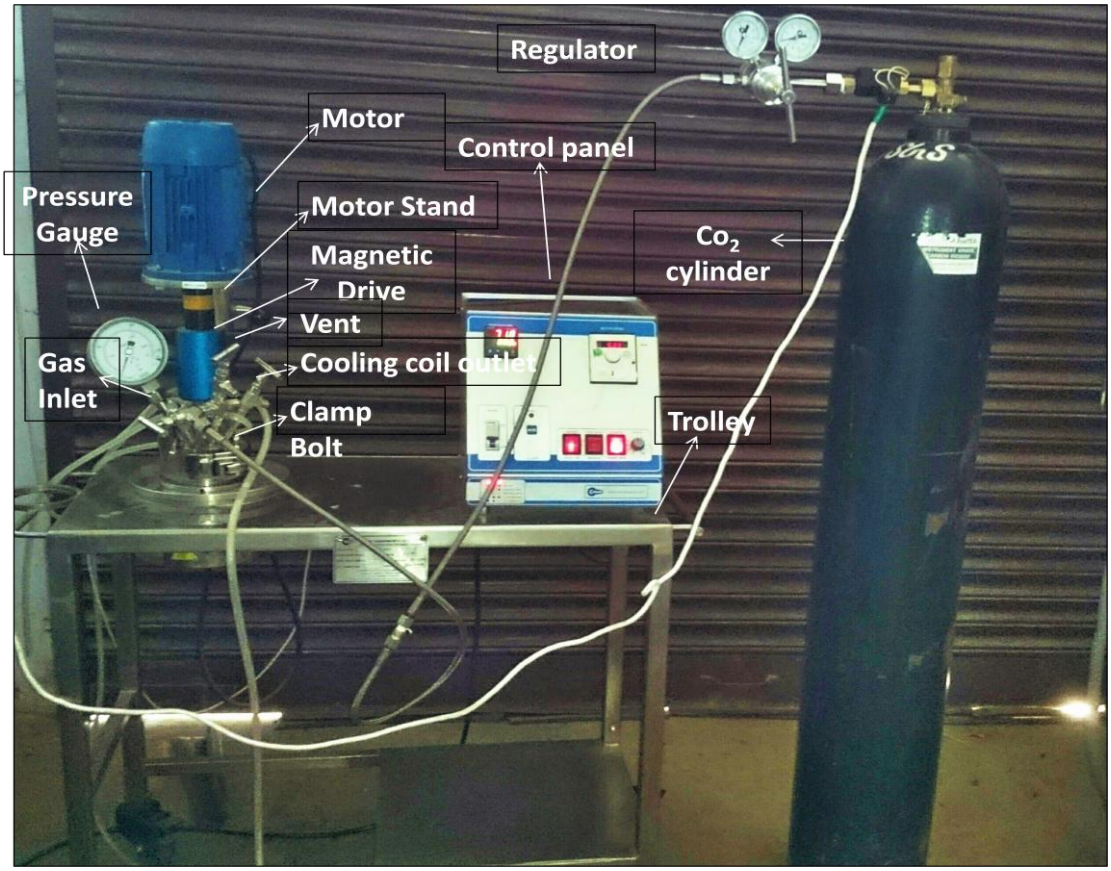


Fig. 4: High pressure reactor used for carboxylation of glycerol

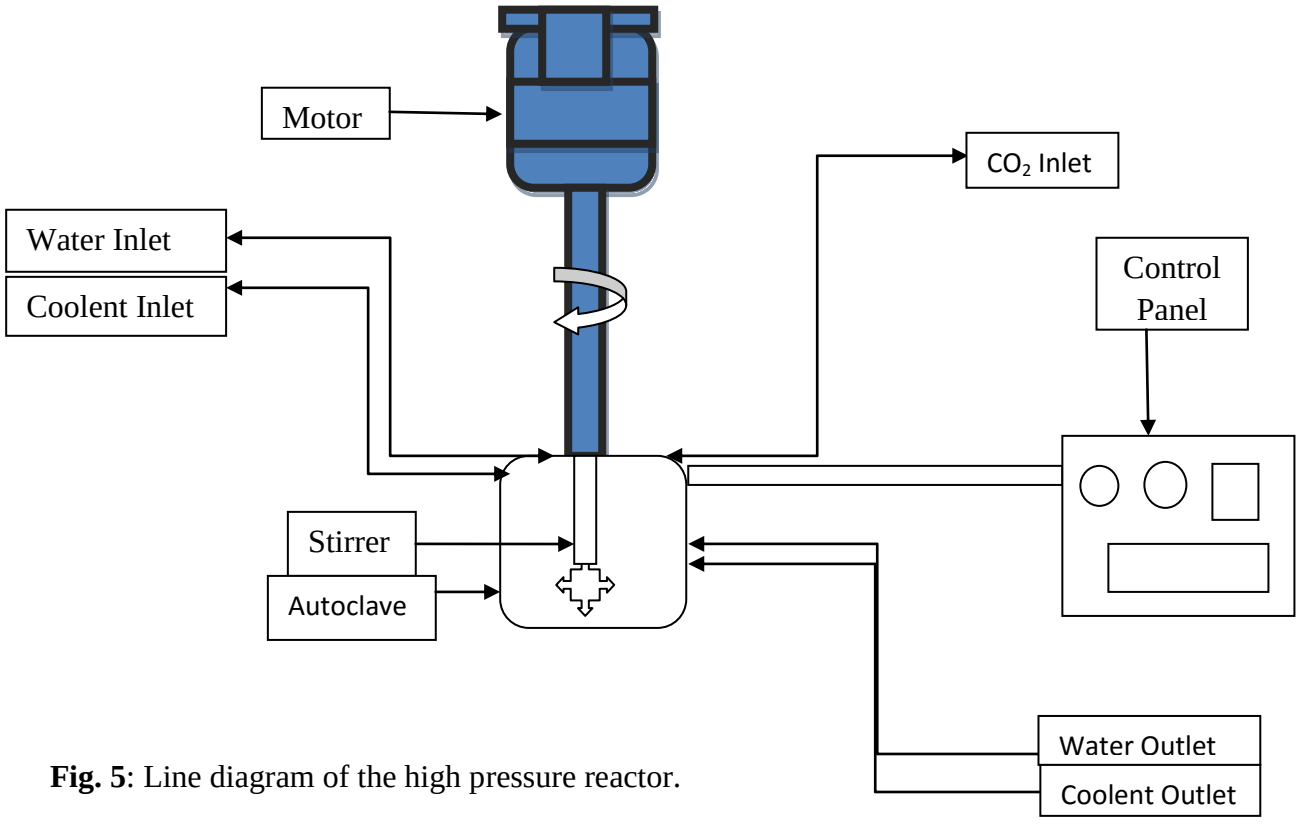


Fig. 5: Line diagram of the high pressure reactor.

Fig. 6: Thin Layer Chromatography analysis of (a) glycerol (R_f = 0.32), (b) reaction mixture (R_f = 0.32), (R_f = 0.56) (c) TEGDME (R_f = 0.56), (d) Glycerol carbonate (R_f = 0.63)

CHAPTER – 3

RESULTS AND DISCUSSION

3.1 CATALYST CHARACTERISATION

3.1.1 Hammett Indicator test

The basicity of CaO is found to be from 9.8-10.1. On loading 10 % Zr on CaO, the basicity increases from 10.1 to 11.1. On further loading 5 % of Li on the base support, the basicity increased from 11.1 to 15.0. Hence, the catalyst was found to be more basic.

3.1.2. SEM

The morphology, size and shape of the Li-Zr/CaO particles were observed by SEM, and the study reveals that 5-Li-Zr/CaO exist as clusters having sharp edges and irregular shaped particles with particle size ranging from 1-2 μm size as shown in Fig. 7. Qualitative analysis of 7-Li-Zr/CaO-700 by EDX study is explained in Table 6 below.

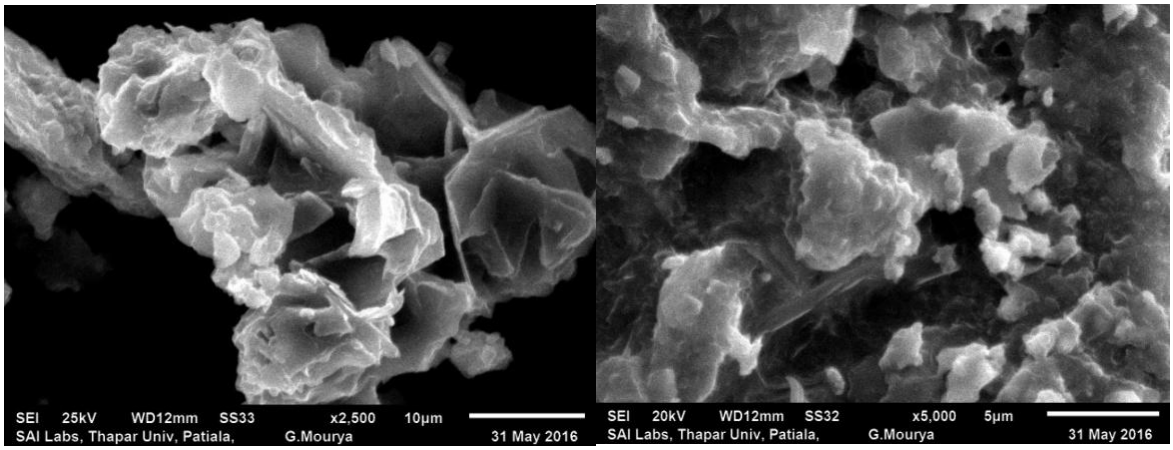


Fig. 7: SEM images of Li-Zr/CaO

Table 6: EDS data of 7-Li-Zr/CaO

Element / Catalyst	Oxygen(wt%)	Lithium(wt%)	Calcium(wt%)	Zirconium(wt%)	Total(%)
Li-Zr/CaO	53.21	2.43	34.46	9.90	100

3.1.3 HRTEM with SAED study

TEM analysis reveals that Li-Zr/CaO particles are actually the clusters of further smaller particles with an average size of ~22.45 nm in quasi-hexagonal shape as shown in Fig. 8. Thus powder XRD as well as TEM study supports the formation of nano structures of Li-Zr/CaO. The SAED pattern from Fig. 8(d) confirms the presence of planes (111) and (200) with d-spacing 3 nm and 4.7 nm. Fig 8(b) shows the inter-planar distance of 0.24 nm.

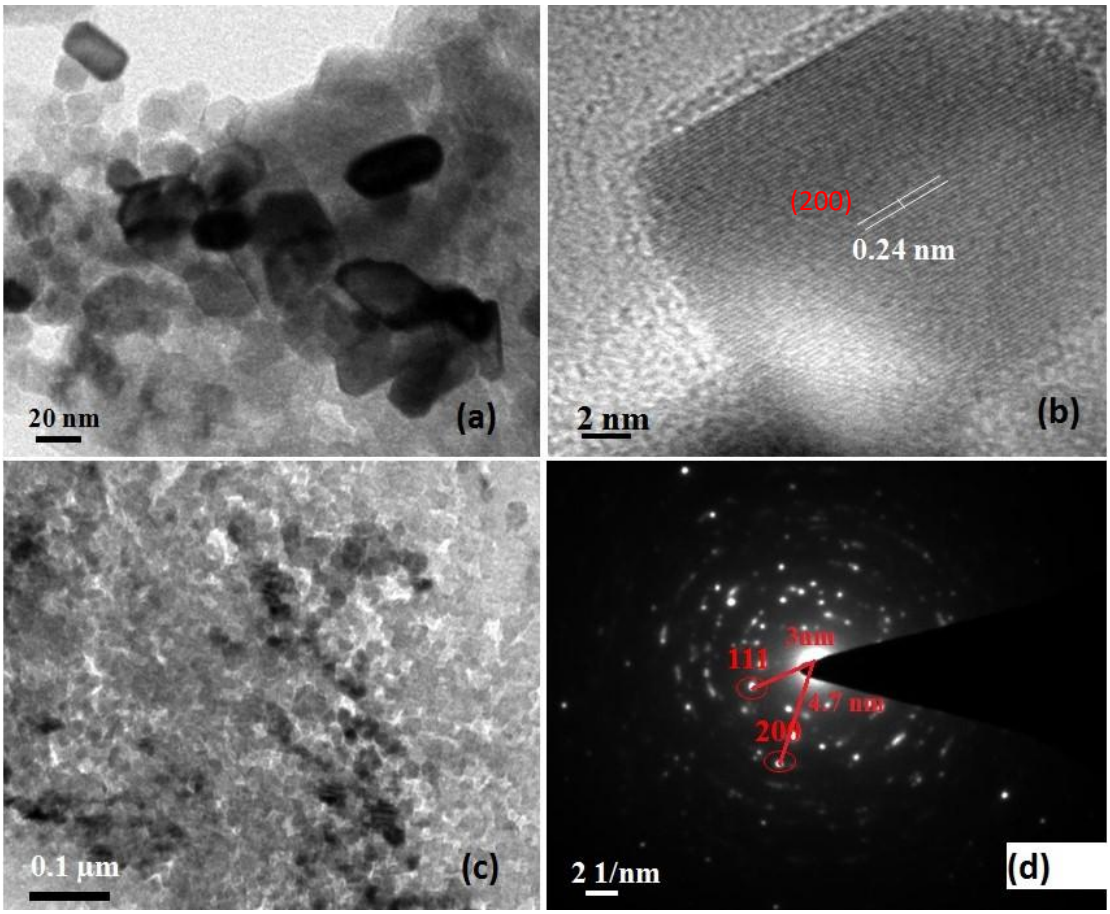


Fig. 8: TEM image of 5-Li-Zr/Cao

3.1.4 XRD

Powder X-ray studies of different metals loaded on the support 10-Zr/CaO have been done and the comparisons are depicted in Fig. 9. The support Zr/CaO showed the characteristic reflections of calcium oxide in cubic (JCPDS 77-2010) and zirconnia in monoclinic form (JCPDS 78-0047). The $CaZrO_3$ mixed oxide complex has also been observed in orthorhombic phase (JCPDS 76-2401). The loading of Zn, Cu and Li on the prepared support shows the addition of new peak pattern corresponding to loaded metal oxides (MO) and $MZrO_3$ (M= Zn, Cu, Li) as descripted in Table 8. Hexagonal phase of $Ca(OH)_2$ has been observed in the case of Li loaded catalyst due to its hygroscopic nature. Moreover cubic phase of $CaZrO_3$ and prominent increase in the orthorhombic ZrO_2 has also been observed and the phases are further explained in Table 8. The number of peaks corresponding to the orthorhombic phase of ZrO_2 has been retained by Li loaded support which lacks in the other Zn and Cu loaded catalysts. Since the size of Cu and Zn is comparable to Ca, hence they form homogeneous solid in CaO.

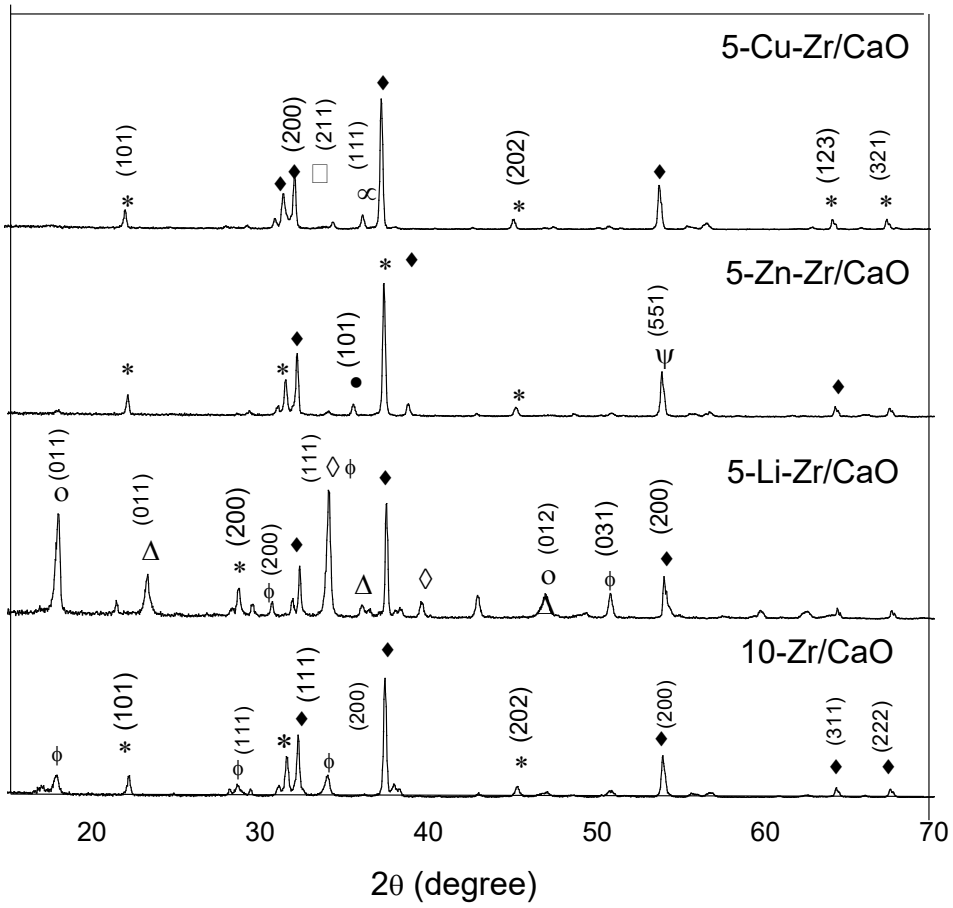


Fig. 9: Powdered XRD patterns of different metals loaded on the same support.

Table 7: Tabulated description of various compounds along with their crystallite size

S.NO:	Symbol	Compound	Structure	Crystallite Size(nm)	JCPDS No.
1	◆	CaO	Cubic	67.18	43-1001
2	✳	$CaZrO_3$	Cubic	43.57	76-2401
3	◯	$Ca(OH)_2$	Hexagonal	55.69	84-1265
4	**Φ**	ZrO_2	Orthorhombic	45.24	83-0809
5	**Ψ**	$ZnZrO_3$	Cubic	46.29	45-0833
6	●	ZnO	Cubic	54.18	89-0510
7	▲	Li_4O_4Zr	Tetragonal	45.65	20-0647
8	◇	Li_2O	Cubic	45.84	73-0593
9	□	$CuZrO_3$	Orthorhombic	58.52	43-0953
10	∝	CuO	Monoclinic	45.94	89-5897

The XRD pattern of 5-Al/Ce is depicted in Fig. 10 which shows alumina peaks in hexagonal phase (JCPDS 02-0921) at 2Θ value of 33.13 and 56.359 degrees. The new peaks upon the addition of ceria was observed at 33.13 corresponding to tetragonal phase of $CeAlO_3$ (JCPDS 81-1186) and at 28.42 and 56.35 degrees corresponding to cubic CeO_2 (JCPDS 81-0792).

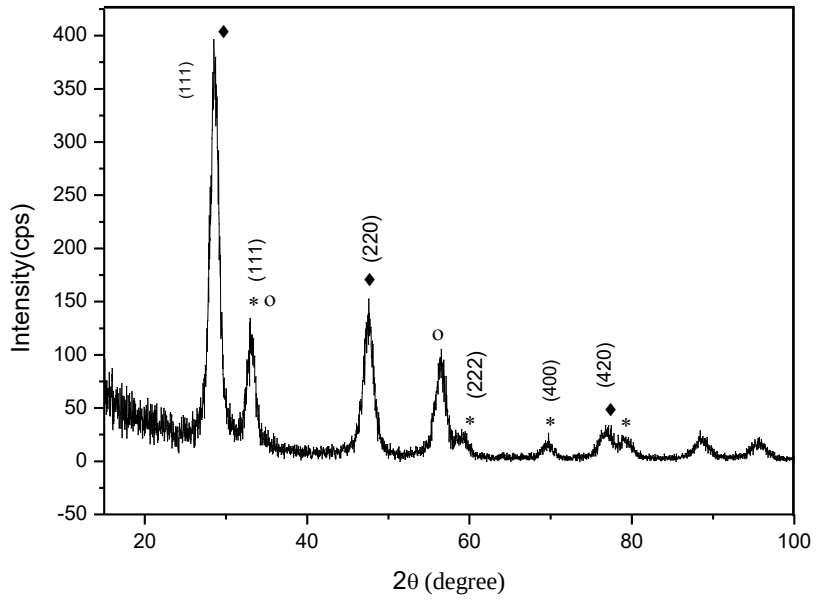


Fig. 10: XRD-graph of 5-Al/Ce catalyst

Table 8: Tabulated description of various compounds along with their crystallite size

S.NO:	Symbol	Compound	Crystallite size(nm)	No:
1	◆	CeO_2	16.06	81-0792
2	✳	$CeAlO_3$	10.32	81-1186
3	◯	Al_2O_3	11.39	02-0921

3.2 BIODIESEL CHARACTERISATION

Proton NMR technique is not only non-destructive but also did not require complicated derivatization and sample preparation procedure for the quantification of products. Therefore for quantification and characterization of FAME, ^{1}H-NMR was employed. The ^{1}H NMR spectrum of CO shows the characteristic glyceridic proton signals at 4.15–4.35 ppm, as shown in Fig.11. On transesterification, same peaks were no longer found in the proton NMR

spectrum of FAME (Fig.11). Moreover, the formation of FAME was further supported due to the appearance of new peaks at 3.6 ppm (singlet).

In ^{13}C-NMR spectrum of CO, signals due to glyceridic carbon appear at 62.2 and 69.0 ppm, as shown in Fig.12. The formation of FAME could also be supported due to the appearance of peaks at 51.4 due to -OCH3 carbons. Further, peaks corresponding to the glyceridic carbons were no longer found in the ^{13}C NMR spectrum of FAME.

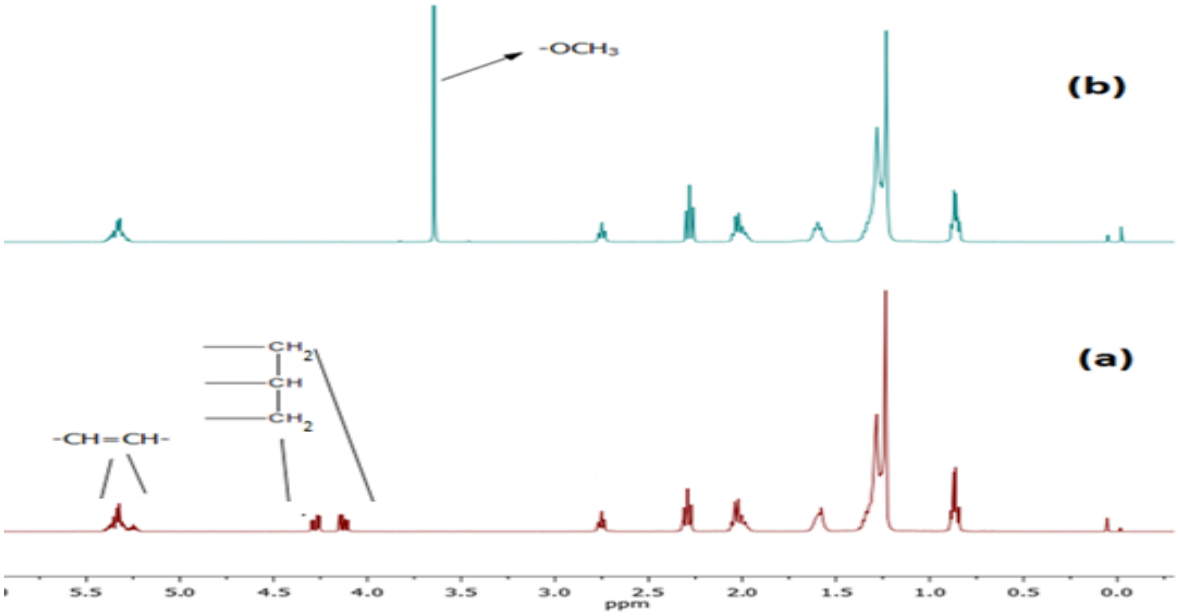


Fig. 11: ^{1}H NMR of (a) cotton seed oil and (b) FAME derived from cotton seed oil

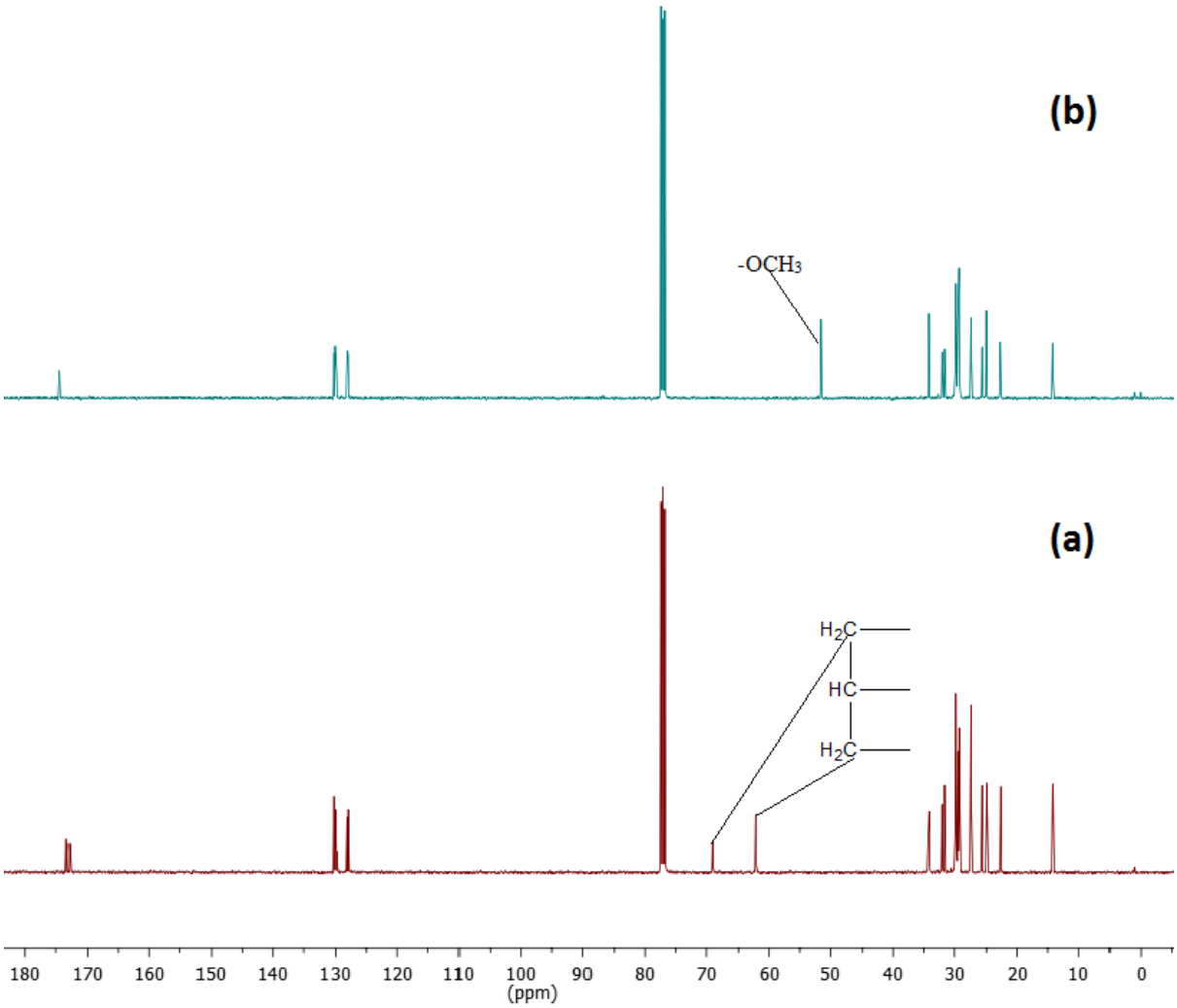


Fig. 12: ^{13}C-NMR of (a) cotton seed oil and (b) cotton seed oil derived FAME.

3.3 CATALYTIC ACTIVITY

In order to optimize the reaction condition for the catalyst to obtain maximum FAME yield during transesterification, following reaction parameters were varied: (i) impregnated zirconium ion concentration on CaO (ii) Different metals loaded on the optimised support (iii) impregnated lithium ion concentration on support Zr/CaO (iii) methanol/oil molar ratio (iv) reaction temperature (v) Effect of moisture on the catalytic activity. Finally, the reusability of the catalyst was also studied and reported. The reaction was carried out in the general manner by keeping a fixed stirring speed of 500 rpm.

3.3.1 Effect of zirconium ion concentration on catalytic activity

In order to test the effect of impregnated Zr ions on the activity of the catalyst, different catalysts were prepared by varying the concentrations of Zr on CaO from 3-12 wt%. The

transesterification reactions of cotton seed oil were performed with 12:1 methanol to oil molar ratio at 65 °C in the presence of 5 wt% of catalyst. The reaction completed in 3 hours with FAME yield >98%. Fig. 13 given below advocates the same by suggesting the activity increases with increase in Zr concentration loaded upto 10 wt%, however a further increase does not affect the activity of the catalyst.

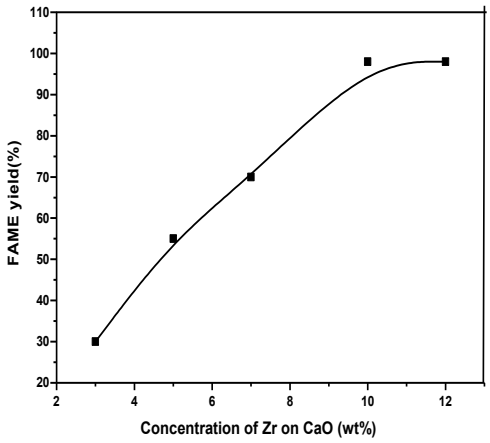


Fig. 13: Effect of Zr concentration on CaO on the FAME (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 1 hour).

3.3.2 Effect of different metals loaded on the support 10-Zr/CaO.

To determine the final metal to be impregnated on the support Zr/CaO, various metals like Li, Zn, Cu were loaded and catalytic activity was checked. Transesterification reactions were performed with methanol to oil molar ratio of 12:1 at 65 °C in the presence of 5 wt% of prepared catalysts (Li-Zr/CaO, Cu-Zr/CaO, Zn-Zr/CaO). Fig. 14 suggests that Li showed maximum amount of activity with reaction duration of 2.5 hours whereas minimum activity was shown by Zn-Zr/CaO.

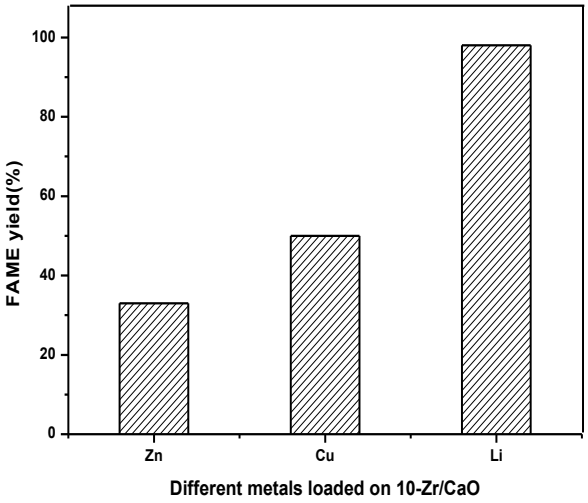


Fig. 14: Effect of different metals on the support Zr/CaO on FAME yield(reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C).

3.3.3 Effect of impregnated lithium ion concentration on 10-Zr/CaO

To determine the optimum amount of lithium ion impregnation in CaO, a series of catalysts by varying the amount of lithium ion from 1 to 12 wt % (metal ion/CaO) in CaO were prepared. The transesterification reaction of cotton seed oil was done with 12:1 methanol to oil molar ratio at 65^{o}C and 5 wt% of catalyst. The reaction was completed in 1 hour with FAME yield of >99%. The biggest advantage of using this catalyst was that it did not leech out in the reaction mixture. Fig. 15 given below shows the increase in catalytic activity from 1 wt% to 7 wt% and then it becomes constant. No further effect of increase in concentration was seen on the catalytic activity.

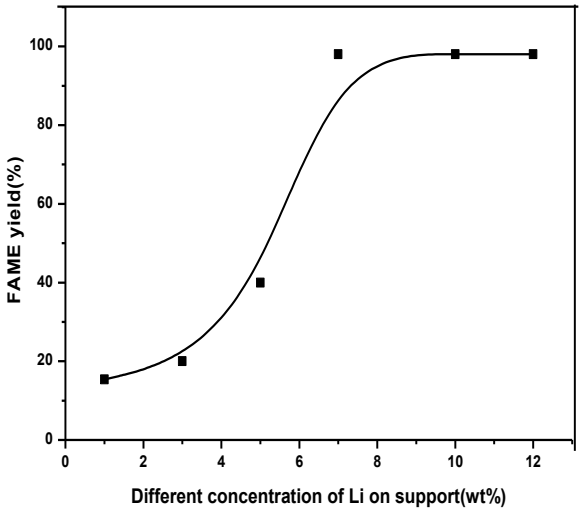


Fig. 15: Effect of Li concentration on the base 10-Zr/CaO on the FAME yield (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C).

3.3.4 Effect of methanol/oil molar ratio

Theoretically as the reaction demands the minimum amount of methanol to oil molar ratio required is 3:1 for 100 % complete transesterification of oils into FAMEs. Therefore, the reaction is always done with excess of alcohol so as to keep the reaction in forward direction since it is a reversible reaction. Alcohol also helps in regenerating the active sites on the catalyst surface by removing product molecules. It increases the rate of reaction as we go on increasing the ratio of methanol to oil. To optimize the correct methanol to oil ratio, reactions were done using the 5 wt% of catalyst Li-Zr/CaO at 65 °C temperature. Methanol/oil ratio was varied from 3:1 to 15:1. As Fig. 16 depicts, FAME yield increased from 60% to 99% by increasing the ratio from 3:1 to 12:1. However, after that there was no effect on the catalytic activity or FAME yield.

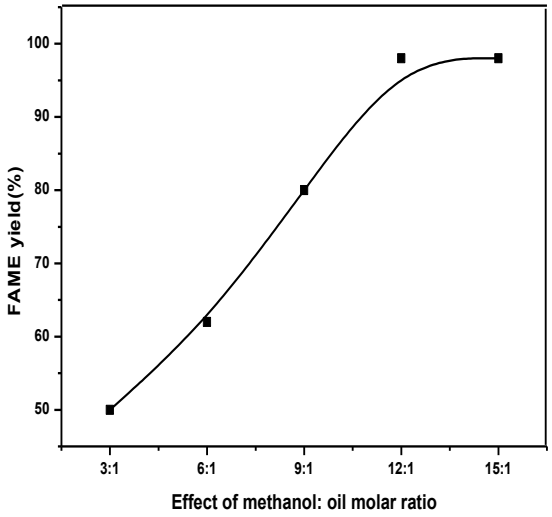


Fig. 16: Effect of methanol to oil molar ratio on the FAME yield (reaction conditions: catalyst amount, 5 wt% of oil; temperature, 65°C; and reaction duration, 1 hour).

3.3.5 Effect of reaction temperature

Since the phase difference of heterogeneous catalysts is different from that of reagents, these catalysts usually require high pressure, temperature and longer reaction period for a good conversion yield. To determine the optimum reaction condition, transesterification of cotton seed oil was performed at different temperature staring from 35°C. The reaction was performed at 12:1 methanol to oil molar ratio with 5 wt% of catalyst Li-Zr/CaO. The temperature was gradually increased from 35 to 65°C. The FAME yield reported increased gradually with rise in temperature. The yield increased till 65°C and did not show any significant increase afterwards. As seen in the Fig. 17, the reaction was also done at room temperature that is 35°C and more, which showed >98% yield of FAME with the reaction completion of time of 4.25 hours. The best temperature however optimised was 65°C which showed the maximum catalytic activity with the reaction time of 1 hour.

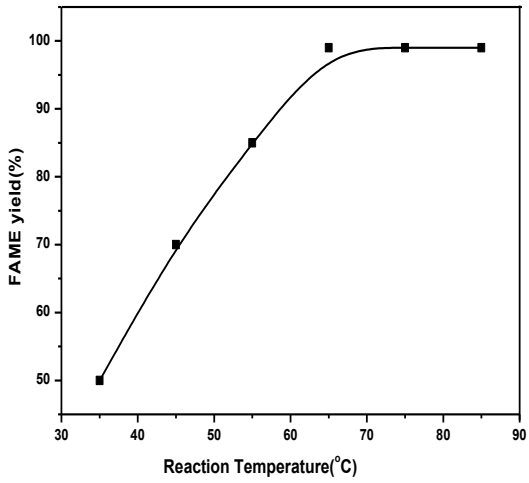


Fig. 17: Effect of reaction temperature on FAME yield (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil).

3.3.6 Effect of the catalyst amount

To find the optimum catalytic concentration, a series of transesterification reactions of Cotton seed oil (CO) with methanol (1:12 molar ratio) were performed in the presence of 1, 3, 5 and 7 wt% (with respect to oil) of Li-Zr/CaO at 65^{o}C temperature. As Fig. 18 shows FAME yield was found to increase as the catalyst concentration was increased from 1 to 7 wt% but further increase in the catalyst loading was not found to affect the FAME yield.

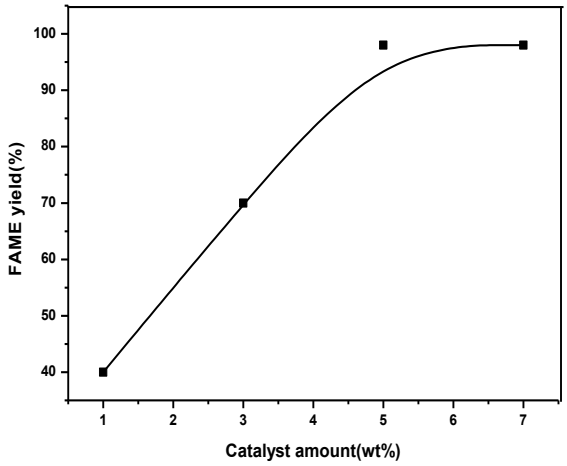


Fig. 18: Effect of the catalyst amount with respect to oil on the FAME yield (reaction conditions: methanol/CO molar ratio, 12:1; temperature, 65 °C; and reaction duration, 1 hour).

3.3.7 Effect of the Moisture on the catalytic activity

Presence of > 0.1 wt% moisture contents in reaction mixture was found to deactivate the homogeneous alkali and acid catalysts. Heterogeneous catalysts, due to immobilized active sites, are expected to demonstrate higher moisture resistance. To prove the moisture resistance of 7-Li-Zr/CaO catalyst, the transesterification reactions of Cotton seed oil were performed by adding up to 6 wt% (water/oil) water in the reaction mixture. As shown in Fig. 19, the catalyst was found to be effective for the transesterification of CO, even in presence of 5 wt% moisture contents. A further increase in moisture contents (> 5 wt%) in the reaction mixture, results in a high degree of catalyst deactivation.

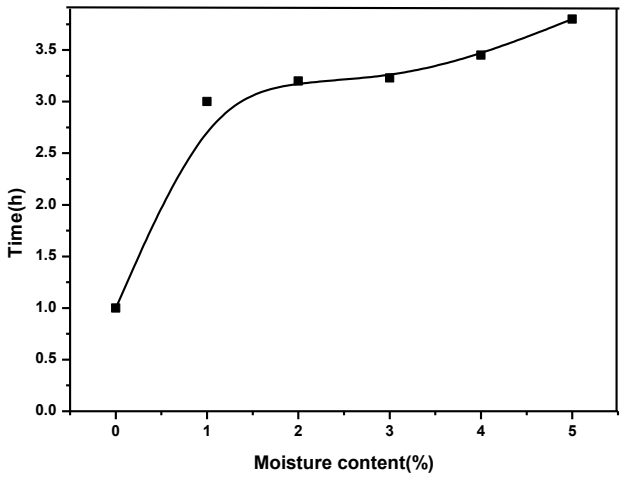


Fig. 19: Effect of the moisture contents on the activity of Li-Zr/CaO catalyst (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C).

3.4 Reusability study

The reusability study of heterogeneous catalyst is done because it is the most important aspect of these catalysts and should be done so as to have a general idea of the overall production cost. To begin with the study, optimized catalyst i.e. 7-Li-Zr/CaO was used for the transesterification of cotton seed oil at the optimum conditions of 65°C with methanol to oil ratio of 12:1. After the completion of the reaction, the reaction mixture was filtered and catalyst was recovered, washed with hexane 4-5 times and once again dried and calcined at 700°C. The catalyst hence recovered was once again used for the reaction and the process was repeated till not enough catalyst was left for a reaction. The study showed that the catalyst showed the activity till 3 successive catalytic cycles. As Fig. 20 shows, the catalyst gave a

yield of >99% of FAME and in the 3rd cycle the yield decreased and the reaction time also increased to 5 hours. The gradual loss of the catalytic activity could be due to the blockage of active sites because of the adsorbed organic molecule.

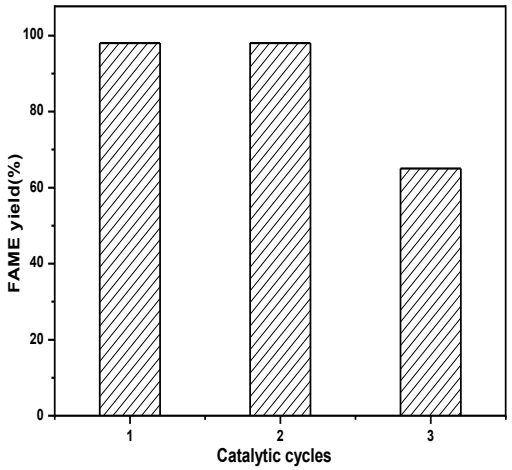


Fig. 20: Reusability studies of 7-Li-Zr/CaO catalyst transesterification of CO (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C).

3.5 Hot filteration test

In order to evaluate the heterogeneous mode of the prepared catalyst, hot filteration test was prformed. The study was done by performing the transesterification reaction of cotton seed oil under the optimised conditions of 12:1 methanol to oil molar ratio using 5 wt% (with respect to oil) of Li-Zr/CaO at 65°C. The reaction was stopped after half an hour and the catalyst was filtered out and completely removed from the reaction mixture. The reaction mixture after catalyst removal was once again heated for another 3 hours. No significant increase in FAME yield was observed during the reaction period to support the true mode of the catalyt.

CHAPTER-4

CONCLUSIONS

CONCLUSIONS

The catalyst, 7-Li-Zr/CaO-700, has been prepared by a wet chemical method in nanocrystalline form as revealed by TEM and powder XRD studies. The same catalyst was found to have the highest basic strength among the prepared catalysts, as supported by the Hammett indicator analysis. The Li-Zr/CaO nanocatalyst was found to be efficient even at room temperature (35 °C) for complete transesterification reactions of triglycerides with methanol. The optimized conditions are methanol/oil molar ratio, 12:1; catalyst concentration, 5 wt%; reaction temperature, 65°C; and reaction duration of 1 hour. The catalyst was found to be effective even for the transesterification of low quality feedstock having up to 5 wt% moisture. Further, the catalyst could be employed during 3 catalytic cycles without significant loss in activity. This catalyst was not found to catalyze the process of carboxylation of glycerol.

REFERENCES:

Alba-Rubio, A. C.; Vila, F.; Alonso, D. M.; Ojeda, M.; Mariscal, R.; Granados, M. L.; *Appl. Catal., B: Environ*. **2010**, 95, 279.

Antunes, W. M.; Veloso, C.O.; Henriques, C. A. *Catal. Today* **2008**, 133, 548.

Aresta , M.; Dibenedetto , A.; Pastore, C.; Cuocci, C.; Aresta, B.; Cometa, S.; De Giglio, E. *Catal. Today* **2008**, 137, 125.

Aresta, M.; Dibenedetto, A.;, Nocito, F.; Pastore, C.; *J. Mol. Catal., A: Chemical* **2006**, 257, 149.

Arzamendi, G.; Campoa, I.; Arguinarena, E.; Sanchez, M.; Montes, M.; Gandia, L. M. *J. Chem. Eng.* **2007**, 134, 123.

Bournay, L.; Casanave, D.; Delfort, B.; Hillion, G.; Chodorge, J. A. *Catal. Today.* **2005**, 106, 190.

Canakci, M.; Gerpen, J. V. *Trans. ASAE* **1999,** 42 (5), 1203.

Cervero , P. J. M.; Coca, J.; Luque, S. *Grasas Y Aceites* **2008**, 59(1), 76.

Clark, J. H.; Budarin, V.; Deswarte, F. E. I.; Hardy, J. J. E.; Kerton, F. M.; Hunt, A. J.; Luque, R.; Macquarrie, D. J.; Milkowski, K.; Rodriguez, A.; Samuel, O.; Tavener, S. J.; White, R. J.; Wilson, A. J. *Green Chem*. **2006**,8, 853.

Claude, S.; Mouloungui,Z.; Yoo,J.W.; Gaset,A. European Patent 0955298, 1996.

Coniglio, L., Coutinho, J. A. P., Clavier, J. Y. *et al.*, Prog. Energy Combust. Sci. 2014, 43, 1.

da Silva, M. J. ; Julio, A. A.; Dorigetto, F. C. S. *RSC Adv*., **2015**, 5, 44499.

Dehkhoda, A. M.; West, A. H.; Ellis, N. *Appl. Catal., A: General* **2010**, 382, 197.

Dehkordi, A. M.; Ghasemi , M. *Fuel Process. Technol.* **2012**, 97, 45.

Deka, D. C.; Basumatary, S.; Lee, J. S. *Biomass Bioenergy* **2011**, 305, 1797.

Dibenedetto, A.; Angelini, A.; Aresta, M.; Ethiraj, J.; Fragale, C.; Nocito, F. *Tetrahedron* **2011**, 67, 1308.

Dorado, M. P.; Ballesteros, E.; Mittelbach, M.; Lopez, F. J. *Energy Fuels* **2004**, 18, 1457.

Encinar, J.M.; Juan, F.; Gonzalez, J.F.; Rodriguez-Reinares, A.; *Fuel Process. Technol*. **2007**, 88(5), 513.

Freedman, B.; Pryde, E. H.; Mounts, T. L. *J. Am. Oil Chem. Soc*. **1984**, 61 (10), 1638.

Fukuda, H.; Kondo, A.; Noda, H. *J. Biosci. Bioeng*. **2001**, 92 (5), 405.

Georgea, J.; Patel, Y.; Muthukumaru Pillai, S.; Munshic, P.; *J. Mol. Catal., A: Chemical* **2009**, 304, 1.

Hama, S.; Yamaji, H.; Kaieda, M.; Oda, M.; Kondo, A.; Fukuda, H. *J. Biochem. Eng.* **2004**, 21, 155.

Hu, S.; Guan, Y.; Wang, Y.; Han, H. *Appl. Energy*. **2011**, 88, 2685.

Jacobson, K.; Gopinath, R.; Meher, L. C.; Dalai, A. K. *Appl. Catal., B: Environ*. **2008**, 85, 86.

Jaya,N. *Fuel Process. Technol*. **2011**, 92, 452. Oguzhan Ilgen

Kouzu, M.; Hidaka, J. *Fuel* **2012**, 93, 1.

Kulkarni, M. G.; Dalai, A. K. *Ind. Eng. Chem. Res*. **2006**, 45, 2901.

Li, X.; Lu, G.; Guo, Y. L.; Wang, Y. Q.; Zhang, Z. G.; Liu, X. H. *Catal. Commun.* **2007**, 8, 1969.

Lotero, E.; Goodwin, Jr. J. G; Bruce, D. A.; Suwannakarn, K.; Liu, Y.; Lopez, D. E. In *Catalysis*; Spivey, J. J.; Agarwal, S. K.; Dooley, K. M., Eds.; Royal Society of Chemistry: United Kingdom, **2006**, 19, 41.

Marchetti, J. M.; Errazu, A. F. *Fuel* **2008**, 87, 3477.

Meher, L.C.; Kulkarni, M. G.; Dalai, A. K.; Naik, S. N.; *J. Lipid. Sci. Technol.* **2006**, 108, 389.

Meher, L.C.; Sagar, D.V.; Naik, S. N. *Renew. Sustainable Energy Rev.* **2006**, 10 (3), 248.

Mohammed, M. M. M.; Elkady, O. A.; Abdelhameed, A.W. *Open Journal of Metal* **2013**, 3. 4.

Monteiro, M.R.; Ambrozin, A.R.P; Liao, L.M.; *Talanta* **2008**, 77, 593.

Ochoa-Gomez, J. R.; Gomez-J-Aberasturi, O.; Maestro-Madurga, B.; Pesquera-Rodriguez, A.; Ramirez-Lopez, C.; Lorenzo-Ibarreta, L.; Lorenzo-Ibarreta, L.; Torrecilla-Soria, J.; Villaran-Velasco, M. C. *Appl. Catal., A: General* **2009**, 366, 315.

Ochoa-Gomez, J. R.; Gómez-J-Aberasturi, O.; Ramirez-Lopeza, C.; Maestro-Madurgaa, B. *Green Chem*. **2012**, 14, 3368.

Patil, P. D.; Gude, V. G.; Reddy, H. K.; Muppaneni, T.; Deng, S.; *Journal of Environmental Protection.* **2012**, 3, 107

Rokicki, G.; Rakoczy, P.; Parzuchowski, P.; Sobiecki, M. *Green Chem*. **2005**, 7, 529.

Su, F.; Guo, Y. *Green Chem***. 2014**, 16, 2934.

Shu, Q.; Gao, J.; Nawaz, Z.; Liao, Y.; Wang, D.; Wang, J. *Appl. Energy* **2010**, 87, 2589.

Shu, Q.; Yang, B. L.; Yuan, H.; Qing, S.; Zhu, G. L. *Catal. Commun.* **2007**, 8, 2158.

Shumaker, J. L.; Crofcheck, C.; Tackett, S. A.; Santillan-Jimenez, E.; Crocker, M. *Catal. Lett*. **2007**, 115, 56.

Tang, Y.; Meng, M.; Zhang, J.; Lu, Y. *Appl. Energy.* **2011**, 88, 2735.

Tudorache, M.; Protesescu, L.; Coman, S.; Parvulescu, V. I. *Green Chem*. **2012**, 14, 478.

Vieville, C.; Yoo, J.W.; Pelet, S.; Mouloungui, Z. *Catal. Lett.* **1998**, 56, 245

Wang, L.; Yang, J. *Fuel* **2007**, 86, 328.

Wang,Y.; Ou, S.; Liu, P.; Xue, F.; Tang, S. *J. Mol. Catal. A: Chem.* **2006**, 252,107.

Xie, W. L.; Li, H. T. *J. Mol. Catal. A: Chem.* **2006**,255, 1.

Xie, W.; Peng, H.; Chen, L. *Appl. Catal., A* **2006**, 300, 67.

Yoo, J.W.; Mouloungui, Z.; Gaset, A. US Patent 6,316,641 B1, 2001.

Yoo, S. J.; Lee, H. S.; Bambang, V.; Kim, J.; Kim, J. D.; Lee, Y. W. *Bioresour. Technol.* **2010,** 10, 8686.