Ni IMPREGNATED Zn/CaO AS HETEROGENEOUS CATALYST FOR TRIGLYCERIDE TRANSESTERIFICATION AND KINETIC MODELLING

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In the partial fulfilment of the requirement for the degree of

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Submitted by:
SACHIN KUMAR
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UNDER THE SUPERVISION OF

Dr. AMJAD ALI	**Dr. RAJ KUMAR GUPTA**
Associate Professor	Associate Professor and Head
School of Chemistry and Biochemistry	Department of Chemical Engineering

SCHOOL OF CHEMISTRY & BIOCHEMISTRY

THAPAR UNIVERSITY
PATIALA-147004
2016

CERTIFICATE

This is to certify that the thesis entitled "**Ni IMPREGNATED Zn/CaO AS HETEROGENEOUS CATALYST FOR TRIGLYCERIDE TRANSESTERIFICATION AND KINETIC MODELLING**" 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. Raj Kumar Gupta**, Associate Professor and Head, Department of Chemical Engineering, Thapar University, Patiala and that no part of this project has been submitted for the award of any other degree.

Sachin

(SACHIN KUMAR)

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
School of Chemistry and Biochemistry
Thapar University
Patiala, 147004

(Dr. RAJ KUMAR GUPTA)
Associate Professor and Head
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 of Academic Affairs,
Thapar University,
Patiala, 147004

CANDIDATE'S DECLARATION

I hereby declare that the work presented in the thesis entitled, **"Ni IMPREGNATED Zn/CaO AS HETEROGENEOUS CATALYST FOR TRIGLYCERIDE TRANSESTERIFICATION AND KINETIC MODELLING"** 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 carried out under the supervision and guidance of **Dr. Amjad Ali**, Associate Professor, School of Chemistry and Biochemistry and **Dr. Raj Kumar Gupta**, Associate Professor and Head, 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 on the basis of any other degree of this or any other university.

Date: July, 04, 2016

Sachin

(SACHIN KUMAR)

Place: Patiala

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

Amjad

(Dr. AMJAD ALI)
Associate Professor,
School of Chemistry and Biochemistry,
Thapar University,
Patiala

(Dr. RAJ KUMAR GUPTA)
Associate Professor and Head,
Department of Chemical Engineering,
Thapar University,
Patiala

(Dr. BONAMALI PAL)
Professor and Head,
School of Chemistry and Biochemistry,
Thapar University,
Patiala.

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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,

Sachin

Place: Patiala

(SACHIN KUMAR)

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ABSTRACT

In present work a series of Ni impregnated Zn/CaO has been prepared by varying the Ni concentration in the range of 2-10 wt% by wet impregnation method. The prepared 7-Ni-Zn/CaO catalyst was characterized by Hammett Indicator, powder XRD, FE-SEM and HR-TEM and TGA studies. This catalyst was employed for the transesterification of triglycerides to yield fatty acid alkyl esters (FAAE) and then for kinetic modelling by LHHW model. ^{1}H-NMR and ^{13}C-NMR techniques were employed to quantify the FAME yield obtained during the transesterification reaction.

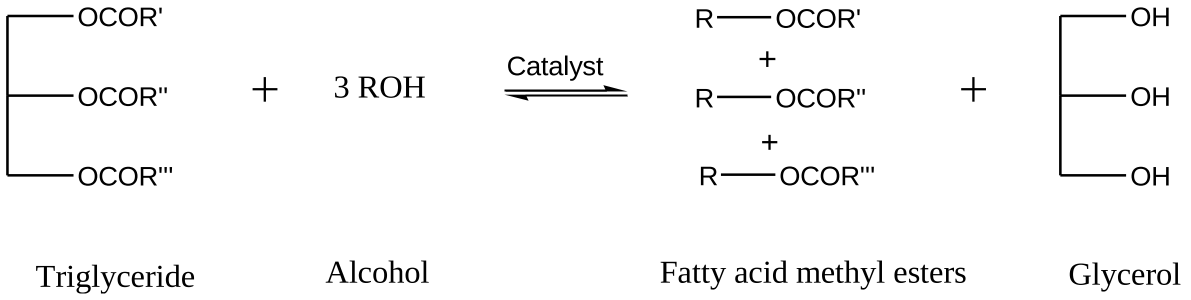
Under the optimized reaction conditions of 5 wt% catalyst (with respect to oil), 65 ºC reaction temperature, methanol to oil molar ratio 9:1, ≥98% FAME yield was obtained in 1.5 h of reaction duration.

CHAPTER 1

INTRODUCTION AND LITERTURE REVIEW

1.1 INTRODUCTION

Due to the steady growth in population as well as industrialization, the demands for fossil fuels are also gradually increasing. Fossil fuel resources are limited, nonrenewable and bound to exhaust, hence, there is need to replace it with renewable sources. Biodiesel defined as a mixture of fatty acid alkyl esters (FAAE) has attained an international attention due to its trait’s like highly degradable, non-toxicity, very low emission of CO (carbon monoxide), particulate matters and unburnt hydrocarbons (Al-Zuhair, 2007). Biodiesel can be produced through four primary ways: direct use and blending of raw oils (Adams *et al.*, 1983), micro emulsions (Schwab *et al.*, 1987), thermal cracking or pyrolysis (Chang and Wan, 1947) and transesterification (Kouzu and Hidaka, 2012). Nowadays, biodiesel is synthesized from trigylcerides (vegetable or animal fats) by its transesterification with alcohol in the presence of catalyst. In transesterification, ester group from waste cooking oils or fats (triglycerides) is separated to form tri alkyl ester molecule as show in Scheme 1.



Scheme 1. Transesterification of the triglycerides and R’, R” and R’” are straight hydrocarbon chain of fatty acids.

The alcohol used in transesterification reaction is methanol due to its cheap cost. New generation biodiesel proposes to originate raw material from algae and other feedstock which provide sustainability to the energy sources desired to adequately complement to the biodiesel industry. Irrespective of feedstock for biodiesel production, a catalyst is required to complete the reaction in significant time. There is a case where catalyst is not required for biodiesel production that is when alcohol and oil are used in supercritical conditions. Catalyst can be synthesized by various methods including thermal pretreatment (Micic *et al.*, 2015), precipitation (co-precipitation) (Teo *et al.*, 2014), impregnation (Kumar and Ali, 2012), sol-gel (Umdu *et al.*, 2009), mechanochemistry (Lukic *et al.*, 2016). But here we prepared catalyst by wet impregnation method. Catalysts are mainly divided into the categories of homogeneous and heterogeneous. Earlier, the biodiesel industry was dominated by the use of homogeneous catalyst due to their simple usage and less requirement of time for conversion of oil to corresponding ester. Enzymes are the other important catalyst possessing high selectivity and also belong to the group of homogeneous catalysts. However, the restriction that lies with their application for making of biodiesel is their somewhat high cost. Cheaper homogeneous acidic or basic catalysts provide high conversion as well as biodiesel yield. However, they require though washing by water and neutralization by respective acids or alkali, resulting the need of more water and generation of more excess waste water. The biodiesel then be dried off to remove the resultant moisture content. However, use of homogeneous catalyst leads to the production of soaps. These limitations thus can be avoided by the use of heterogeneous catalysts that can eliminate the additional running costs associated with the stages of separation and purification. In addition, heterogeneous catalyst doesn’t produce soap through FFA (free fatty acid) neutralization and triglyceride (vegetable oils or animal fats) saponification. For a catalyst to be heterogeneous in nature, it shouldn’t leach into the reaction mixture and should be reused. The catalyst should be highly selective for the desired product formation and should give high biodiesel conversion and yield. Efficiency of heterogeneous process depends upon several variables such as type of oil, methanol to oil molar ratio, temperature and type of catalyst. Biodiesel can be used in conventional compression engines and also in most modern diesel engines in pure form or in form of blend with the petroleum diesel fuel (Szybist *et al.*, 2007). Blends of biodiesel are designated by “B” followed by volume % e.g. B5 and B20, consisting of 5% and 20% biodiesel in petroleum diesel respectively. So it can be used as heating oil and fuel (Mushrush *et al.*, 2001).

1.2 LITERATURE REVIEW

Transesterification reaction of vegetable oils or animal fats can be carried out *via* catalytic or non-catalytic approach. In case of non-catalytic approach, there is a no need of catalyst reaction takes place under supercritical conditions which are an energy exhaustive process (Coniglio *et al.*, 2014) and require high temperature and pressure. A catalytic process involves biocatalyst (lipase) and chemical catalyst. The selection of the catalysts depends on the quantity of free fatty acids (FFA) existing in the oils. For oils having low FFA content basic catalysts like (NaOH, KOH, $KOCH_3$, etc.) are preferred while for those oils having high FFA content, acid catalyzed (HCl, H_2SO_4 etc.) esterification trailed by transesterification in presence of alkaline catalyst which is suitable.

1.3 TYPES OF OILS

For the making of biodiesel there are no technical limitations concerning the use of vegetable oils or animal fats. Yet, there are favored vegetable oils with high free fatty acid (FFA) content and whose widespread production is significant.

Oil can be broadly divided into two categories animal fat and vegetable oil. Oils, consequently, are fluid at room temperature, so that their usage as diesel fuel depends chiefly on their viscidness. Furthermore, animal fats, because of higher content of saturated free fatty acids are solid at room temperature, and can’t be used in the diesel engines in its original form. Though it isn’t common to use blends of vegetable oils with diesel in dissimilar proportions, depending on the viscidness of oil, these mixtures can be used in diesel engines. Animal fats haven’t been considered to the similar level as vegetables oils, however there are selected works about poultry fat used to produce biodiesel, e.g. Oil from algae, bacteria and fungi also has been examined (Hernando *et al.*, 2007).

“First-generation” biodiesel is derived from edible feedstock like canola, tailed by sunflower, soybean and palm oil etc. (Korbitz, 1998); however, biodiesel production from refined vegetable oils is impractical and uneconomical due to high feedstock cost and priority as food resources. “Second-generation” biodiesel is produced from inedible feedstock, which is competitive for the commercial use of biodiesel production because of their low price and high yield. Nevertheless, these low-grade virgin plant oils generally contain a high content of FFAs and water as well as trace salts, which may interfere with the biodiesel production process. Therefore, rational design of novel and efficient catalysts for biodiesel production from inedible feedstock is important.

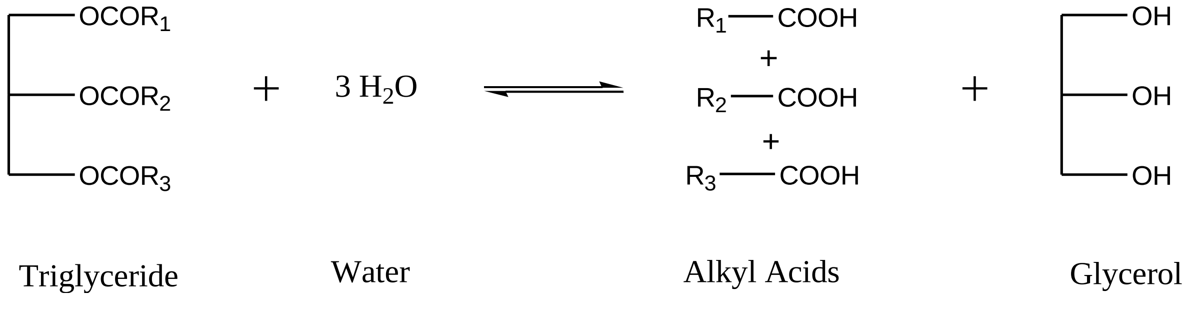
In addition to vegetable oils and animal fats, further materials such as frying oils (waste cooking oil) have been used for biodiesel production; however, some changes in the reaction procedure often have to be made due to the existence of water or free fatty acids (FFA) in the biodiesel (Bockisch, 1998).

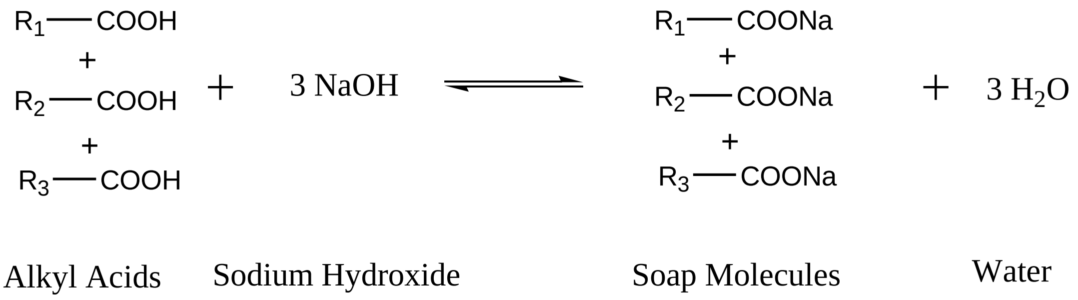
1.4 CATALYSTS

Acidic, basic and enzymatic catalysts can be used for transesterification reaction. Acid and base catalyzed reactions are further divided into homogeneous and heterogeneous categories. In enzyme catalyzed transesterification methods, oil with high acids content can be used and glycerol formed as a byproduct can be recovered smoothly. Also, there is no side reaction produced in this case, however, due to high cost of enzymes it isn't economical viable at commercial level (Silva *et al.*, 2007)

1.4.1 Homogeneous Catalysts:

At industrial level biodiesel is produced by mainly utilizing homogenous alkali catalysts like NaOH, KOH etc., for transesterification reactions. The chief advantage of utilization of homogeneous alkali catalysts is their high activity even at ambient conditions, lesser cost and freely availability. However, these catalysts are extremely sensitive to water content (> 0.1 wt%) and FFA content (>0.6 wt%) existing in feedstock. Formation of soap takes place due to high water content as shown in Scheme 2, which lessens the ester yield and the separation of glycerol from methyl ester becomes difficult due to increase in viscidness and emulsion formation (Liu, 1994; Basu and Norris, 1996).

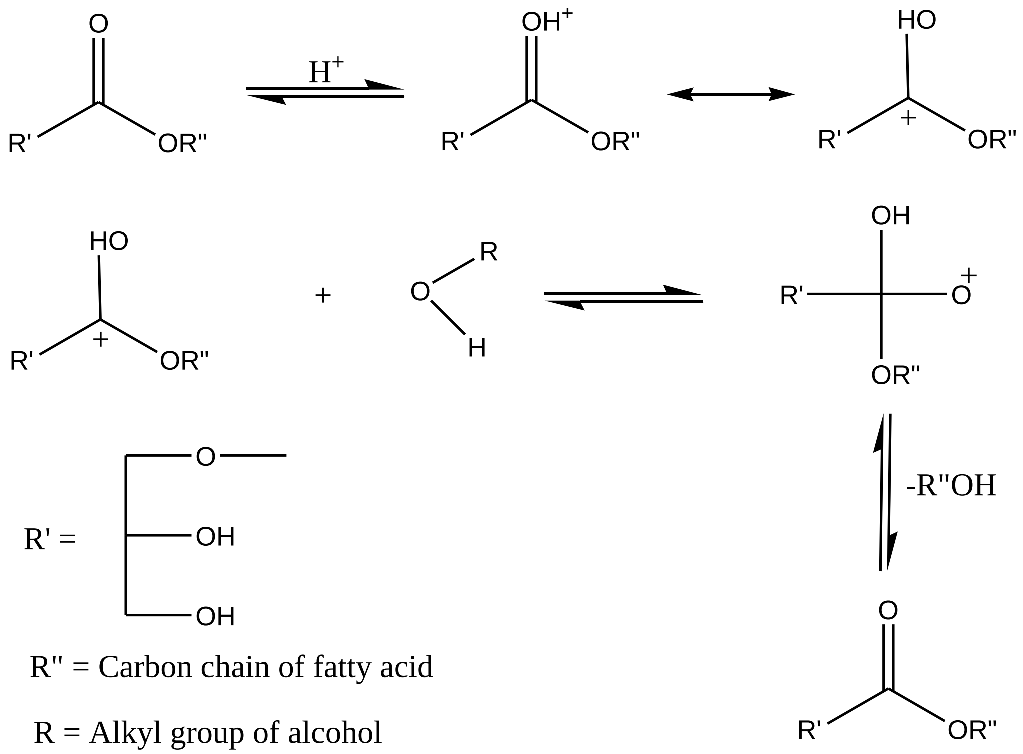




Scheme 2. Saponification of fatty acids in presence of alkali, where R_1, R_2 and R_3 = straight hydrocarbon chains of fatty acid**.**

1.4.1.1 Homogeneous Acidic Catalysts:

The shortcomings of homogenous alkali catalysts might be evaded by means of homogeneous acid catalysts like H_2SO_4 (sulphuric acid), HCl (hydrochloric acid) (Wang *et al.*, 2006). They are generally active for the transesterification of vegetable oils or animal fats having more than 1% FFA (free fatty acids) contents (Freedman *et al.*, 1948). They normally need punitive circumstances as compared to homogeneous base catalysts such as high temperature, high molar ratio of methanol to oil and long reaction interval. Acid catalysts are generally used for the two-step transesterification of feed stocks with free fatty acid (FFA) content greater than 1 wt%. In 1st step acid catalyst is used for esterification of FFA with alcohol (mainly methanol) followed by acid neutralization and then transesterification by base catalyst. The mechanism of acid catalyzed transesterification reaction is shown in Scheme 3.



R" = Carbon chain of fatty acid

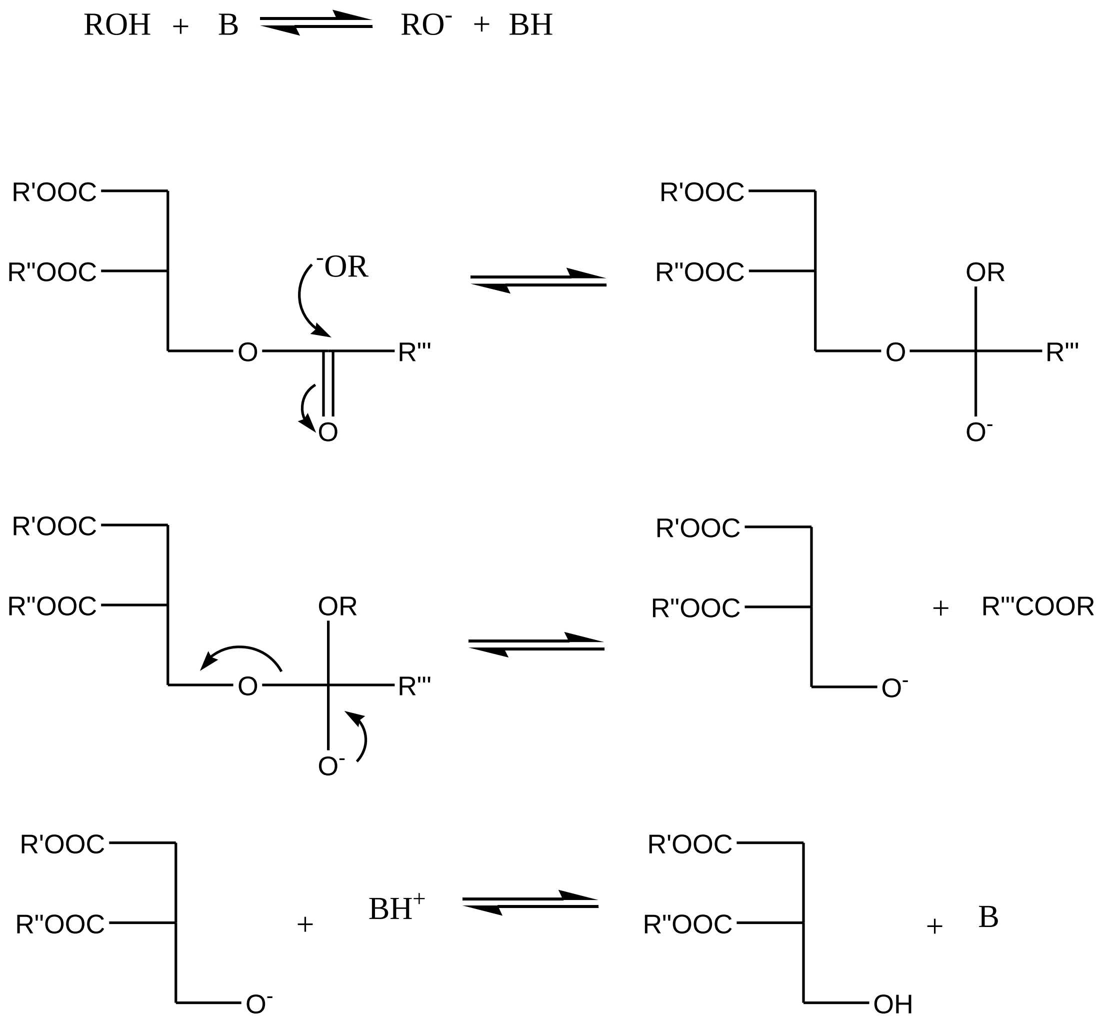
R = Alkyl group of alcohol

Scheme 3. Mechanism of acid catalyzed transesterification of vegetable oils or fats.

The major problem with acid catalysts is their less reactivity and deactivation by water, which is adjacent product through the acid catalyzed esterification reaction. Furthermore, it causes the erosion of the reactor and therefore, costly acid resistance reaction container is essential.

1.4.1.2 Homogeneous Basic Catalysts:

Few scholars stated the comparison of NaOH and KOH catalysts and their activity too. Dorado *et al*, (2002) concentrated on biodiesel production using different kind of vegetable oils like palm oil, animal fat, Spanish olive oil and a mix of German vegetable oil and KOH as catalyst in a two-step reaction. Their yield was reported as 89-95%. The two-step reaction process is superior than single-step because it needs a lower temperature for reaction, less methanol and catalyst amount and obtained a higher yield (Cayh and Kusefoglu, 2008). The mechanism of homogeneous base-catalyzed transesterification reaction is displayed in Scheme 4.



Scheme 4. Mechanism of base catalyzed transesterification of vegetable oils or fats where R is the alkyl group of alcohol and R’, R” and R”’ are the hydrocarbon chains of fatty acids.

Both homogeneous acidic and basic catalysts must be counteracted at the end of the reaction and detached from the products through washing with water which generates vast amount of industrial wastes.

1.4.2 Heterogeneous Catalysts:

In direction to overcome the difficulties accompanying with homogeneous catalysts, research has been concentrated for the development of heterogeneous catalyst.

Heterogeneous catalysts have numerous benefits over homogeneous catalysts such as they can be recovered from the reaction mixture easily, recyclable, and lead to the formation of non-contaminated product and hence the product washing is not necessary.

Broadly heterogeneous catalysts can be divided into two categories: heterogeneous base and heterogeneous acid catalysts. Numerous methods have been used for the preparation of heterogeneous catalysts for the transesterification process. These includes: calcination, pyrolysis synthesis, physical mixing, wet impregnation and co-precipitation. To attain high catalytic activity for transesterification reaction blend of these methods has been used. But, the utmost used combination for catalyst preparation with high catalytic activity for transesterification reaction is impregnation monitored by calcination (Kaur and Ali, 2014).

1.4.2.1 Heterogeneous Acid Catalysts:

Heterogeneous acid catalysts have the power to replace sturdy liquid acids to eradicate corrosion problems and the resulting environmental risks modeled by liquid acids (Helwani *et al.*, 2009). Some researchers have prospered in converting biodiesel from waste cooking oil (WCO) using these catalysts. Lou *et al.* (2008) used carbohydrate derivative solid acid catalysts, which are insoluble in the tried solvents and liquid reactants (water, methanol, n-hexane, t-butanol, oleic acid and WCO). The carbohydrate derived catalysts prepared beneath improved conditions exhibited much higher activities than typical sulfated zirconia (Jitputti *et al.*, 2006) and niobic acid for both esterification and transesterification. Starch derived catalysts are highly effective in converting high free fatty acids (FFA) containing waste oils to biodiesel by simultaneous esterification and transesterification. The starch derived catalysts are very effective in producing biodiesel of about 92 % after 8 hours from waste oils (WO) containing 27.8 wt% FFA content. This catalyst has very brilliant operational steadiness and has potential as a heterogeneous acid catalyst.

Jacobson *et al.* (2008) discovered the best solid acid catalyst for the simultaneous transesterification and esterification reactions. Zinc stearate ($Zn(C_{18}H_{35}O_2)_2$) immobilized on silica gel was found to be the most dynamic and stable heterogeneous catalyst under the enhanced conditions of reaction temperature of 200 ºC, stirring speed of 600 rpm, molar ratio of oil to alcohol is 1:18, and 3 wt% catalyst with respect to oil, producing a maximum ester yield of 98%. Georgogianni *et al.* (2009) studied the transesterification reaction of soybean frying, in the existence of different heterogeneous catalysts (Mg MCM-41, Mg-Al hydrotalcite, and K^+ impregnated zirconia), using low frequency ultra-sonication (24 kHz) and magnetic stirring of 600 rpm for the production of biodiesel. In particular, Mg-Al hydrotalcite exhibited the highest conversion of 97 %. Park *et al.* (2008) used WO_3/ZrO_2 catalyst for transesterification of waste cooking oil (WCO). The highest conversion obtained was 85% in packed bed reactor; optimized condition was 75 ºC reaction temperature and 20 hrs. of reaction time.

1.4.2.2 Heterogeneous Base Catalysts:

Different type of heterogeneous base catalysts have been stated in literature for the transesterification reactions including supported solid base catalyst such as KI/Al_2O_3 (Xie *et al.*, 2006), Eu_2O_3/Al_2O_3 (Li *et al.*, 2007), calcium oxide (Yan *et al.*, 2008), MgAZr (Li *et al.*, 2011), nano-magnetic $KF/CaO\text{-}Fe_3O_4$ (Hu *et al.*, 2011) and modified CaO by trimethyl chlorosilane (TMCS) (Tang *et al.*, 2011). Guo *et al.* (2010) explored the use of sodium silicate as solid base catalysts for the transesterification to achieve 95% yield at optimized condition of 3 wt% catalyst, 7.5:1 molar ratio of methanol to oil, 60 °C reaction temperature, 1 hr reaction time and mixing intensity of 250 rpm.

The mixed oxide synthesized catalysts comprising of CaO and ZrO_2 with various Ca to Zr molar ratios were used for the transesterification of waste cooking oil (WCO) as feedstock with methanol to produce biodiesel at 65 °C and 1 atm pressure. The experimental results specified that the activity of synthesized catalysts raises as the Ca to Zr molar ratio increases but at the same time the firmness of the catalysts decreases. Under the optimized transesterification conditions at 65 °C reaction temperature, catalyst loading of 10 wt.%, methanol to oil molar ratio was 30:1, and reaction time was 2 hrs., a biodiesel yield of 92.1 % could be attained over the $CaO\text{-}ZrO_2$ catalyst with a Ca to Zr molar ratio of 0.5. Other results acquired in this experiment showed that synthesized catalysts can be used as recyclable, stable and active catalysts for the production of biodiesel from waste cooking oil (WCO) (Dehkordi and Ghasemi, 2012).

Melero *et al.* (2014) unceasingly produced biodiesel from waste cooking oil (WCO) on a packed bed reactor. They used the agglomerated Zr-SBA-15 material with bentonite clay to form a macroscopic structured catalyst with particle size of 1.5 mm. The Zr-SBA-15/bentonite catalyst in pellet form was highly active in the continuous flow reactor. It can produce a FAME yield of 96 % at 210 ºC and 70 bar pressure with methanol to oil molar ratio of 50:1 and reaction time of 30 min.

A contrast of transesterification activity of few literature reported heterogeneous catalysts is presented in Table 1.

Table 1. Different solid catalysts and their performances in biodiesel synthesis:

Catalyst	Vegetable Oil	Reaction Temp. (ºC)	M:O	Catalyst amount (wt%)	Reaction Time (hr)	FAME yield (%)	Reference
CaO	Sunflower	252	41:1	5	0.25	99	Reddy *et al.*, 2006
K-Pumice	Sunflower	55	20:1	-	2	99.5	Borges and Diaz, 2013
MgO,MgO/Al_2O_3	Soybean	180	12:1	5	1	92	Cantrell *et al.*, 2005
Mg-Al-CO_3 hydrotalcite	Waste oil	120	24:1	6	6	>90	Brito *et al.*, 2009
Li/Al hydrotalcites	Soybean	65	15:1	3	2	90	Corma *et al.*, 2005
CaO & ZrO_2 mixed oxides	Waste cooking	65	30:1	10	2	92.1	Dehkordi and Ghasemi,2012
K_2CO_3/Al_2O_3	Triolein	65	25:1	6	1	94	Xie and Huang, 2006
Sr/ZrO_2	Palm	115.5	29:1	2.7	1.5	79.7	Omar and Amin, 2011
KOH/Sodium zeoloite	Soybean	65	10:1	3	8	85	Suppes *et al.*, 2004
CaO/AC	Waste palm	60	25:1	-	8	94	Buasri *et al.*, 2012
KF/ZnO	Soybean	65	10:1	5	9	87	Xie and Li, 2006
Calcium ethoxide	Sunflower	80	12:1	3.5	2.5	80.5	Anastopoulos *et al.*, 2013
PbO	Soybean	215	7:1	-	2	89	Singh and Fernando, 2008
La/zeolite	Soybean	160	14.5:1	-	4	48.9	Shu *et al.*, 2007
Zr-SBA-15/bentonit	Waste cooking	210	50:1	-	0.5	96	Melero *et al.*, 2014
$CaTiO_3$,$CaMnO_3$	Rapseed	60	6:1	-	10	90	Kaishima *et al.*, 2008

M:O = Methanol to oil molar ratio; - = Not reported

Thus the literature reported heterogeneous solid catalysts either required high methanol to oil molar ratio, high reaction temperatures and even more reaction durations for significant FAME yield. Also, the catalysts show poor reusability due to leaching of active species from the catalysts support.

1.5 KINETIC STUDY

Usually, the kinetic study of transesterification reactions was done by pseudo first order reaction mechanism. Kumar and Ali, (2012); Kaur and Ali, (2014) reported their kinetic study through pseudo first order reaction mechanism.

In present work, in order to prepare reusable and heterogeneous catalyst for the transesterification of waste cooking oil (WCO), mixed metal oxide of Ni-Zn/CaO was prepared by wet impregnation method.

The kinetic modelling of transesterification reaction was done by LHHW model using dual site, single site and stoichiometric mechanisms.

CHAPTER 2

OBJECTIVES

2.1 OBJECTIVES

1) To prepare mixed metal oxide as heterogeneous solid catalyst for transesterification of triglyceride by wet impregnation method.
2) To characterize the catalyst by Hammett indicator, powder XRD, FE-SEM, HR-TEM, TGA techniques.
3) To study the kinetics of reaction by LHHW model.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 MATERIALS

Waste Cooking Oil (WCO) was bought from local restaurants of Patiala, Calcium Oxide (CaO) (Reagent Grade from Sigma Aldrich), Zinc Nitrate Hexahydrate ($Zn(NO_3)_2.6H_2O$) (AR Grade from Loba Chemie), Nickel Nitrate Hexahydrate ($Ni(NO_3)_2.6H_2O$ (Reagent Grade from Loba Chemie), Hexane (C_6H_{14}) (from Spectrochem Pvt. Ltd.), Ethyl Acetate ($C_4H_8O_2$) (from Loba Chemie), and Methanol (CH_3OH) (from RANKEM) were used directly without any further changes in them. Silica gel G for TLC (Thin Layer Chromatography) was purchased from Loba Chemie.

3.2 METHODS

The basic strength of the catalysts (pK_{BH+}) was obtained by using **Hammett indicator** test. Approximately 100 mg of the catalyst was shaken with 5 mL 0.02M Hammett indicators solution, prepared in methanol to observe the colour change. The Hammett indicators used were:
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).

Powder X–ray diffraction **(XRD)** frameworks were chronicled on a PANalytical's X'Pert Pro diffractometer operating at 40kV using nickel filtered monochromatic Cu Kα radiation (λ=1.54060 Å) by skimming the samples over a 2θ range of 5–80° at the scanning speed of 2°/min.

Field emission scanning electron microscopy united with energy dispersive X–ray spectrometry **(FESEM–EDX)** was executed on JEOL JSM 6510LV. For analysis, initially sample was ultrasonicated in ethanol for 2 h. A drop of this suspension was mounted on a sample holder with the help of carbon tape. The sample was then sputter coated with gold and visualized with instrument to assess the particle morphology.

High Resolution Transmission electron microscopy **(HR-TEM)** with SAED (Selected area (electron) diffraction) pictures of the sample were chronicled on **Tecnai G2 20**, 200 KeV FEI instrument. For sample preparation, powdered sample was assorted with hexane and ultrasonicated for 1 hour to dangle the particles in solvent. A very small volume of this suspension was cited on a copper grid and solvent was parched prior to the analysis.

Fourier transform-infrared **(FT-IR)** spectra of the samples were recorded in KBr accessory on Agilent Cary-660 spectrophotometer in the range of 400-4000 cm^{-1}.

Fourier transform-nuclear magnetic resonance **(FT-NMR)** spectra of waste cooking oils and FAAE's were Chronicled on a JEOL ECS-400 (400 MHz) spectrophotometer in $CDCl_3$ solvent using Tertramethyl silane (TMS) as inner reference and chemical shifts (δ) were stated in parts per million (ppm).

3.3 CATALYST PREPARATION

Catalyst support, Zn/CaO, was prepared using wet impregnation method. In a typical preparation method, CaO (10g) was draped in 40 ml of deionized water. To this, 10 ml of aqueous solution of zinc nitrate of 0.32 M concentration was added to obtain 7 wt% Zn loading over CaO. The slurry so attained was stirred for 3 h, then dehydrated at 120 ºC for 12 h in oven and finally calcined in muffle furnace at temperature 550 ºC for 12 h to obtain 7-Zn/CaO.

The prepared 7-Zn/CaO was employed as support for the Ni impregnation. 10g of 7-Zn/CaO was draped in 40 ml of deionized water. To this, 10 ml of aqueous solution of nickel nitrate of 0.1 M concentration was added to obtain 2-10 wt% Ni^{+2} loading in Zn/CaO. The slurry so attained was stirred for 4 h then dehydrated at 120 ºC for 12 h in oven and finally calcined in muffle furnace in temperature range of 200-900 ºC for 4 h.

The catalysts thus prepared was categorized as x-Ni-Zn/CaO-T, where x and T nickel concentrations (wt %) and calcination temperature (ºC), respectively.

3.4 TRANSESTERIFICATION OF WASTE COOKING OIL (WCO)

Transesterification is a reversible reaction, and hence to force the reaction in the forward direction, an extra amount of alcohol is added. The alcohol to oil molar ratio of stoichiometry reaction is 3:1, to produce 3 moles of biodiesel and 1 mole of glycerol. Usually, the transesterification reactions were carried out in 50 ml double neck round bottom (RB) flask furnished with water cooled reflux condenser, magnetic stirrer and oil bath. In a transesterification reaction, 10g of waste cooking oil with 5 ml of methanol and 0.25 gm catalyst were stirred (600 rpm) at 65 ºC temperature to get a suitable yield (>99%). The development of reaction was observed by withdrawing the sample from the reaction mixture after every 15 min with the help of a dropper and centrifuged to separate the catalyst from the supernatant. The liquid thus obtained was diluted with hexane and was subjected to TLC. TLC was developed using hexane/ethyl acetate in 90:10 v/v as mobile phase and silica gel used as stationary phase. Production of biodiesel was identified by comparing its R_f value (Retention Factor) with methyl oleate ($C_{19}H_{32}O_2$) standard as shown in Fig. 1.

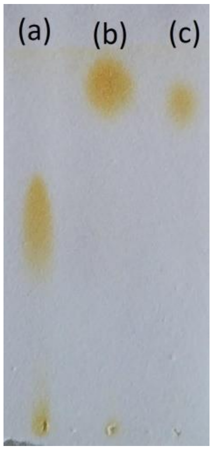


Fig.1. TLC analysis of (a) waste cooking oil (Rf = 0.4), (b) waste cooking oil derived FAME (Rf = 0.7) and (c) methyl oleate standard (Rf = 0.7).

The FAME yield was calculated by ^{1}H-NMR (proton nuclear magnetic spectroscopy) using literature stated method (Knothe, 2001; Gelbard *et al.*, 1995)

$$\% \text{ FAME yield} = [2I_{(\text{methoxy})}/3I_{(\text{methylene})}]\times100$$

where $I_{(\text{methoxy})}$ and $I_{(\text{methylene})}$ are the areas of methoxy protons (3.6 ppm) and methylene protons (2.33 ppm) respectively in the proton nuclear magnetic spectra of FAMEs. An inaccuracy of ±2% was detected when the FAME yield was computed by above method.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CATALYST CHARACTERIZATION

4.1.1 Hammett Indicator Test:

The basic strength (pK_{BH+}) of the pure CaO was found to be in the range of 9.8-10.1 and it was increased gradually from 9.8-10.1 to 10.1-11.1 as the concentration of Zn^{+2} in CaO was increased. On further doping of Ni^{+2} on 7-Zn/CaO (calcined at 550°C), the basic strength was increased from 10.1-11.1 to 11.1-15.

4.1.2 Powder X-Ray Diffraction Study (XRD):

XRD patterns of 7-Zn/CaO and Ni-Zn/CaO prepared by varying nickel concentrations (5−10 wt%) at 550 °C calcination temperature were compared as shown in Fig.2. The XRD of Zn/CaO shows typical diffraction patterns of CaO in the cubic phase (average crystallite size = 60.75nm) (JCPDS 77-2376), and peak corresponding to the ZnO in hexagonal phase (average crystallite size = 49.20nm) (JCPDS 79-0206). Upon Ni loading, new diffraction peak at 29.43° support the formation of rhombohedral phase of $CaNi_4O_8$ (average crystallite size = 45.88nm) (JCPDS 86-2474) while peak at 43.35° support the formation of NiO (average crystallite size = 38.02nm) (JCPDS 89-3080) phase. With the increase in nickel concentration in catalyst support the amount of rhombohedral NiO phase gradually increases.

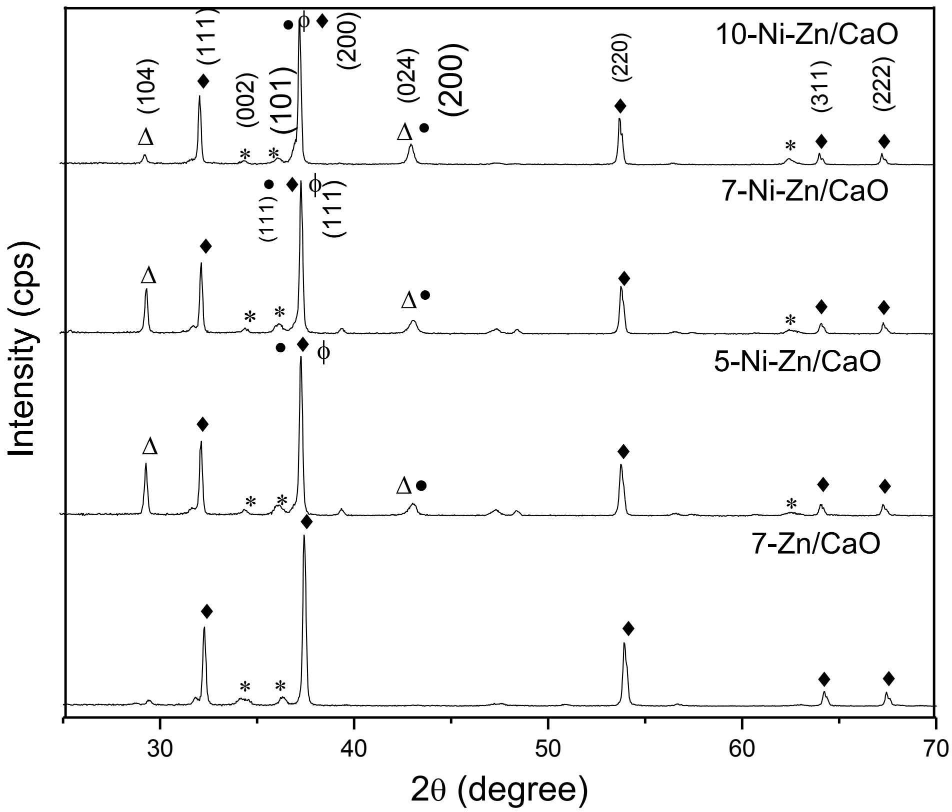


Fig.2. Comparative XRD patterns of 7-Zn/CaO and Ni-Zn/CaO with a variation of Ni^{+2} concentration (5-10 wt %) **(**♦ = calcium oxide; ∗ **=** zinc oxide**;** **Δ** = calcium nickel oxide**;** ● **=** nickel oxide**;** **ϕ** = nickel zinc oxide**)**

4.1.3 SEM-EDS Study:

The size, shape, and morphology of the 7-Zn/CaO and 7-Ni-Zn/CaO particles were observed by SEM as shown in Fig.3, the same study reveals that 7-Zn/CaO exists as irregular flocculent particles having needle shape ending with average size 1-3 µm.

7-Ni-Zn/CaO exists as cluster of cubes distributed irregularly having size 2-5 µm.

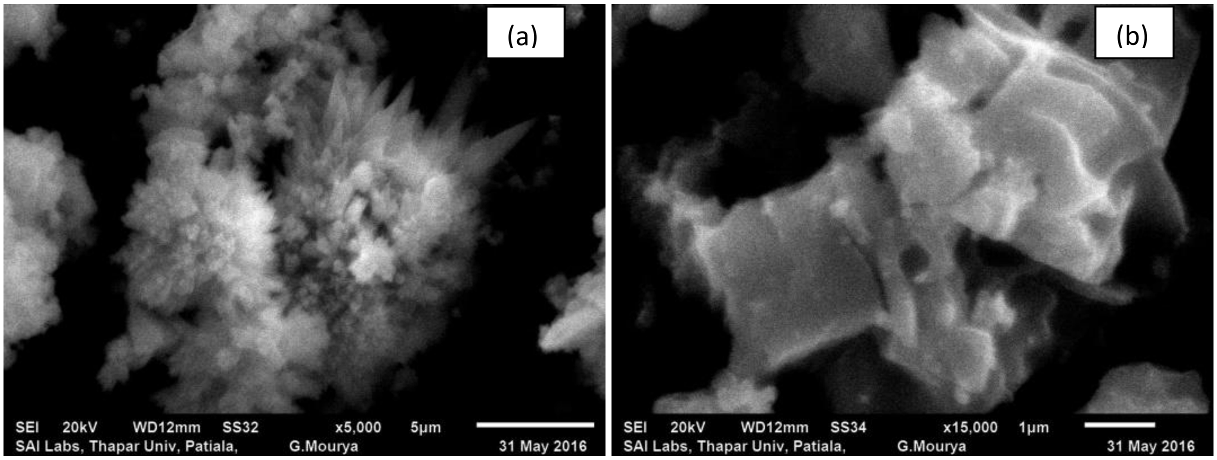


Fig.3. SEM images of (a) 7-Zn/CaO and (b) 7-Ni-Zn/CaO

Qualitative analysis of 7-Zn/CaO and 7-Ni-Zn/CaO by EDX study supports the presence of 6.29 wt% Zn^{+2} and 5 wt% Ni^{+2} as shown in Table 2.

Table 2: EDS Data of 7-Zn/CaO and 7-Ni-Zn/CaO

Elements Catalysts	Oxygen (wt %)	Calcium (wt %)	Zinc (wt %)	Nickel (wt %)
7-Zn/CaO	62.86	30.85	6.29	
7-Ni/Zn/CaO	68.09	25.80	10.36	5.00

4.1.4 HR-TEM with SAED Study:

HRTEM images of 7-Zn/CaO and 7-Ni-Zn/CaO were shown in Fig.4 and Fig.5, respectively.

HR-TEM analysis reveals that Zn/CaO particles are actually the clusters of smaller particles with an average size of ~40 nm of irregular shape. The SAED pattern also confirms the plane 111 (d-spacing = 6.4 nm) and 200 (d-spacing = 4 nm) (Fig.4) and that of Ni-Zn/CaO particles are porous clusters of smaller particles with an average size of 46.8 nm in quasi-hexagonal shape. The SAED pattern also confirms the plane 111 (d-spacing = 2.4 nm) as shown in Fig.5.

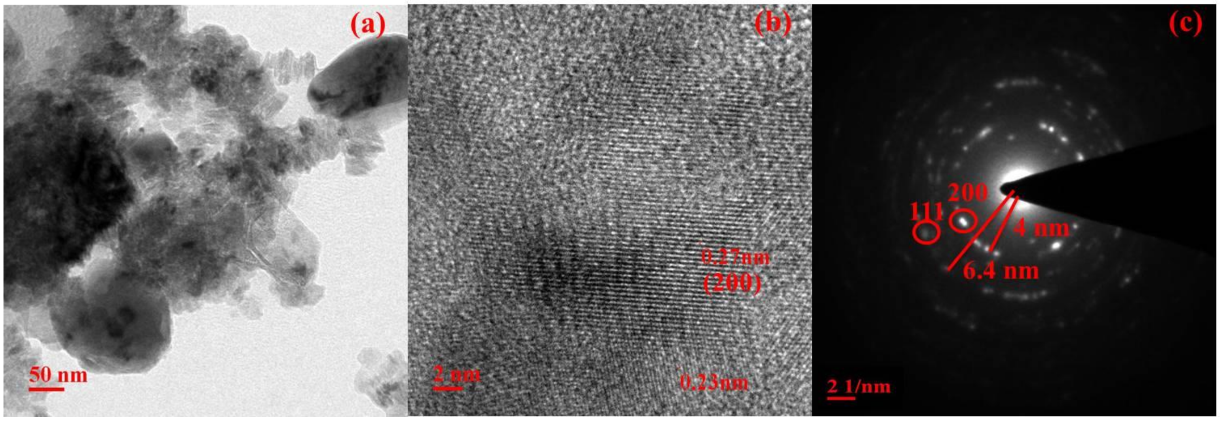


Fig.4. HRTEM images of 7-Zn/CaO (a) dark supports signify the presence of zinc on CaO, (b) lattice fringes of catalyst and (c) SAED pattern.

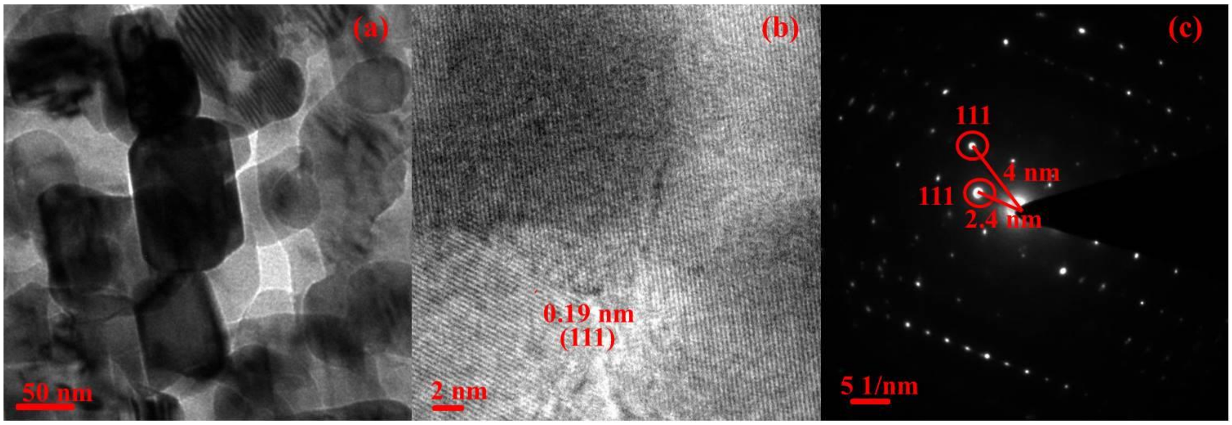


Fig.5. HRTEM images of 7-Ni-Zn/CaO (a) dark supports signify the presence of nickel on Zn/CaO, (b) lattice fringes of catalyst and (c) SAED pattern.

4.1.5 Thermogravimetric Analysis (TGA):

Thermogravimetric curve of uncalcined 7-Zn/CaO and 7-Ni-Zn/CaO catalysts are illustrated in Fig.6, which shows four and three weight loss regions, respectively. The first slight weight loss region 100-190ºC for both curves corresponds to the water evaporation and dehydration of respective nitrate precursors. The second weight loss region 350-430 ºC in Zn/CaO shows the decomposition of nitrate. The third region of 430-546 ºC in Zn/CaO indicates the decomposition of zinc and calcium hydroxide phases into respective oxides. The last region upto 700 ºC shows $CaCO_3$ decomposition which may form due to the reaction of surface CaO with atmospheric CO_2.

The second region 400-600 ºC of Ni-Zn/CaO corresponds to the decomposition of nickel nitrate. The last region upto 700 ºC shows $CaCO_3$ decomposition which may form due to the reaction of surface CaO with atmospheric CO_2.

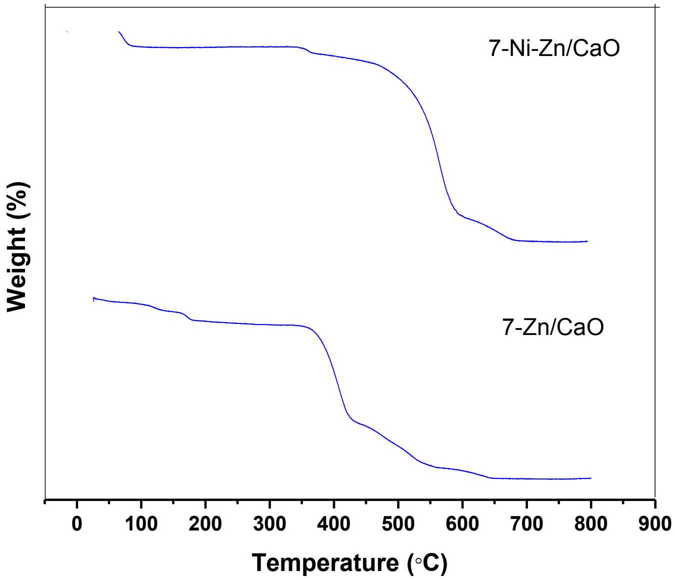


Fig.6. TGA curves of 7-Zn/CaO and 7-Ni-Zn/CaO

4.2 BIODIESEL CHARACTERIZATION

Proton NMR technique is not only non-destructive but also did not require complicated derivatization and sample preparation procedure for the quantification of products. Moreover, this technique could also be used for the structural elucidation of the product molecule. Hence, in present work ^{1}H NMR technique is employed for the FAME quantification and characterization. The ^{1}H NMR spectrum of WCO shows the characteristic glyceridic proton signals at 4.15–4.35 ppm, as shown in Fig.7. On transesterification, same peaks were no longer found in the proton NMR spectrum of FAME. 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 WCO, signals due to glyceridic carbon appear at 62.2 and 69.0 ppm, as shown in Fig.8. The formation of FAME could also be supported due to the appearance of peaks at 51.4 ppm due to $-OCH_3$ carbons. Further, peaks corresponding to the glyceridic carbons were no longer found in the ^{13}C NMR spectrum of FAME.

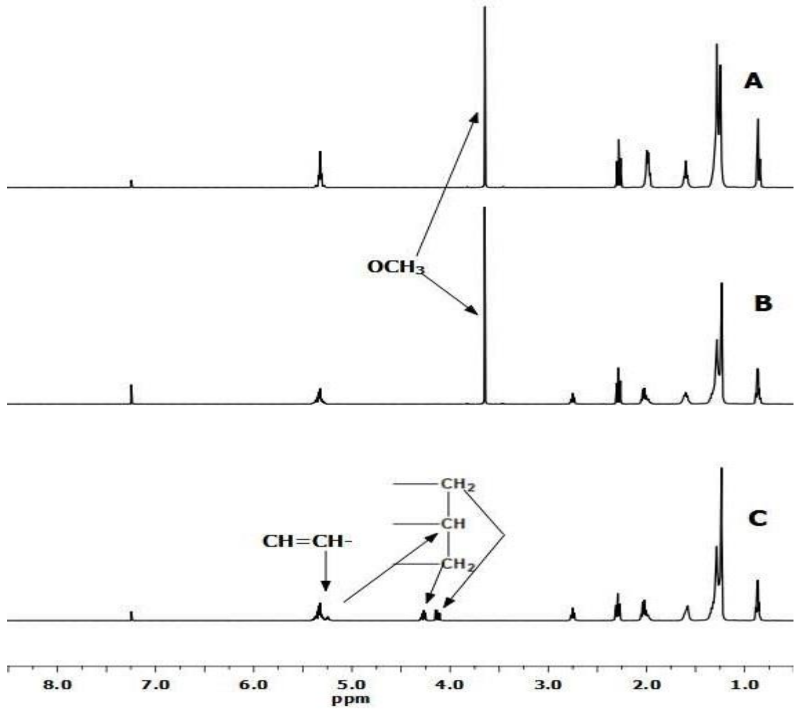


Fig.7. Comparison of ^{1}H-NMR spectra of (a) 7-Ni-Zn/CaO derived FAME, (b) 7-Zn/CaO derived FAME and (c) waste cooking oil.

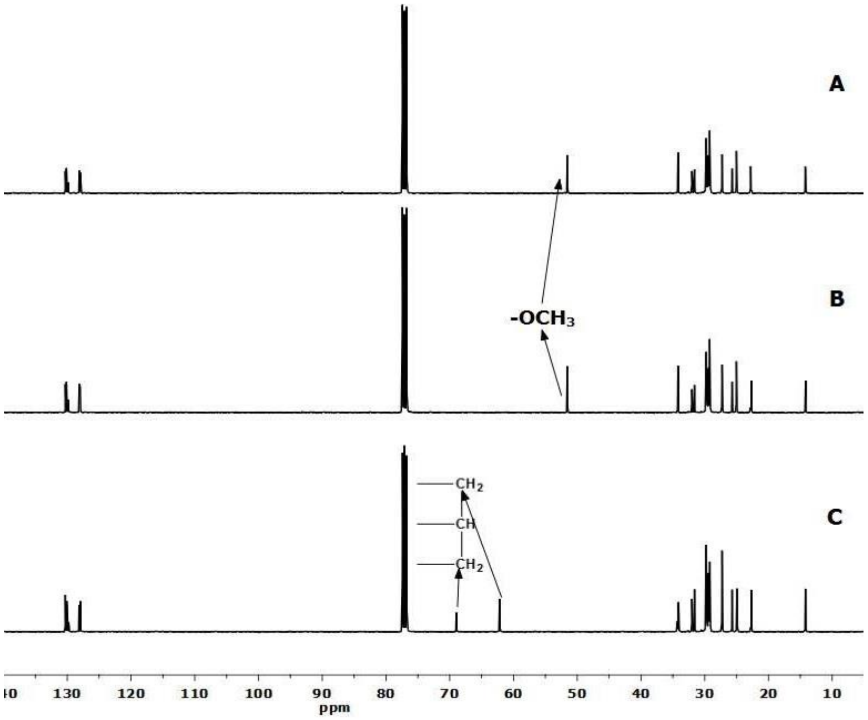


Fig.8. Comparison of ^{13}C-NMR spectra of (a) 7-Ni-Zn/CaO derived FAME, (b) 7-Zn/CaO derived FAME and (c) waste cooking oil.

4.3 CATALYTIC ACTIVITY

Among various concentrations of Zn^{+2} in CaO 7 wt% was found to give the maximum yield but the calcination time was long so to reduce the calcination timings and increase the FAME yield Ni^{+2} was impregnated over the prepared 7-Zn/CaO. So, to optimize the reaction conditions for optimum catalytic activity, transesterification reaction has been carried out at 600 rpm stirring speed by varying one parameter at a time out of following: (i) Ni^{+2} concentrations in Zn/CaO (ii) catalyst amount with respect to oil (iii) methanol/oil molar ratio (iv) reaction temperature and (v) amount of moisture contents present in feedstock. The reusability of the catalyst was also studied.

4.3.1 Effect of the impregnated Ni^{+2} concentrations in Zn/CaO:

To determine the optimal amount of nickel impregnation on Zn/CaO, a series of catalysts were prepared by varying the amount of nickel ion from 2 to 15 wt% on Zn/CaO. The transesterification of waste cooking oil was performed with methanol to oil molar ratio of 9:1 at 65°C in the presence of 5 wt% of the prepared catalysts with respect to oil and for reaction duration of 1.5hr. Fig.9, suggest that up to 7 wt% increase in the Ni^{+2} concentration was found to enhance the activity of the Ni-Zn/CaO catalyst. However, further increase in the Ni^{+2} concentrations has not influenced activity of Ni-Zn/CaO on transesterification of waste cooking oil.

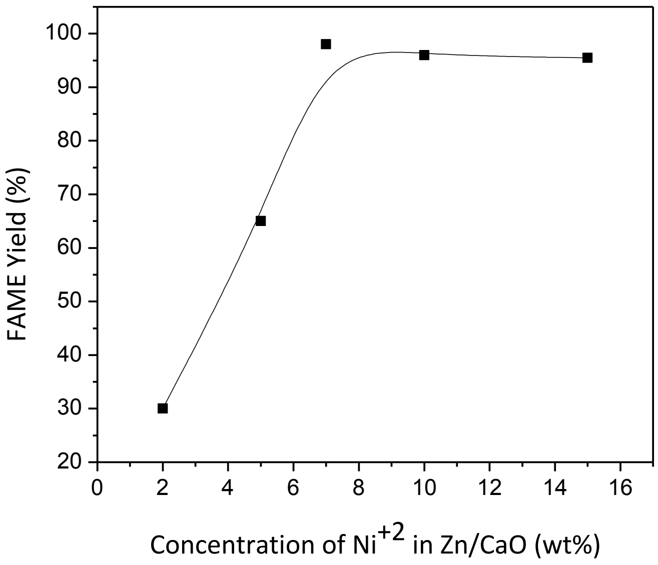


Fig.9. Effect of Ni^{+2} concentrations in Zn/CaO on the FAME (reaction conditions: methanol/WCO molar ratio, 9:1; catalyst amount, 5 wt% with respect to oil; temperature, 65 °C; and reaction duration, 1.5 hours).

4.3.2 Effect of the catalyst amount:

To find the optimal catalyst concentration, a series of transesterification reactions of waste cooking oil with methanol to oil molar ratio 9:1 were performed in the presence of 2-8 wt% (with respect to oil) of 7-Ni-Zn/CaO-550 for 1.5 hours. The FAME yield was found to increase as the catalyst concentration was increased from 2 to 5 wt%. But, further increase in the catalyst loading (>5 wt %) was not found to change the FAME yield significantly as shown in Fig.10. This could be due to the fact that at higher catalyst loading reaction mixture becomes more viscous which could repel the mass transfer in the liquid–liquid–solid system (Taufiq-Yap *et al*., 2011).

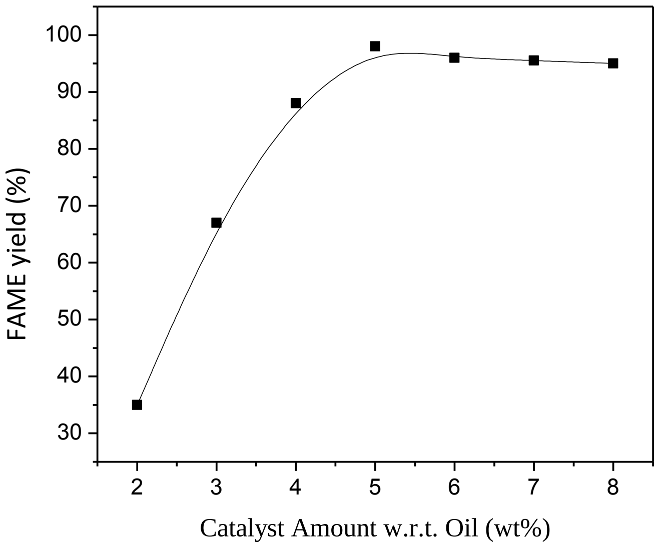


Fig.10. Effect of the catalyst amount with respect to oil on the FAME yield (reaction conditions: methanol/WCO molar ratio, 9:1; temperature, 65 °C; and reaction duration, 1.5 hours).

4.3.3 Effect of methanol to oil molar ratio:

The effect of the methanol/oil molar ratio on the transesterification reaction is an important parameter which affects the FAME yield as well as the cost of biodiesel production. The theoretical methanol to oil molar ratio should be 3:1 for the complete conversion of oil to FAME. However, transesterification being a reversible reaction usually performed with excess of methanol to shift the equilibrium in forward direction to achieve maximum FAME yield (Wang *et al.*, 2011). To determine the optimal methanol/oil molar ratio for 7-Ni-Zn/CaO-550 catalyst, the reactions were performed by varying the methanol/oil molar ratio from 5:1 to 15:1 for 1.5 hours at 65°C. The FAME yield increases from 25 to 98% on increasing methanol/oil molar ratio from 5:1 to 9:1, and further increase in molar ratio was not found to influence the FAME yield significantly as shown in Fig.11.

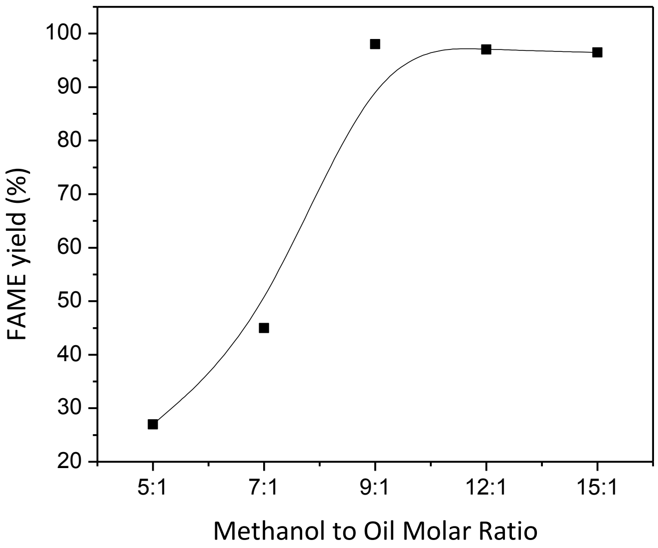


Fig.11. Effect of methanol to oil molar ratio on the FAME yield (reaction conditions: catalyst amount, 5 wt% with respect to oil; temperature, 65 °C; and reaction duration, 1.5 hours).

4.3.4 Effect of reaction temperature:

Heterogeneous catalysts, because of the phase difference from reagents, usually required a high temperature and pressure and longer reaction period to give the significant conversion. To optimize the reaction temperature, the transesterification reaction of waste cooking oil with methanol to oil molar ratio of 9:1, 5 wt% of 7-Ni-Zn/CaO-550°C with respect of oil was carried out at different temperature. The FAME yield was found to increase regularly as the reaction temperature was increased from 35 to 65°C and a further increase in the reaction temperature was not found to influence the FAME yield significantly as shown in Fig.12. Although the catalyst was found to be more effective at 65°C, however, even at the room temperature (35 °C), >90% conversion of WCO into corresponding FAMEs was achieved in 7 hrs. of reaction duration.

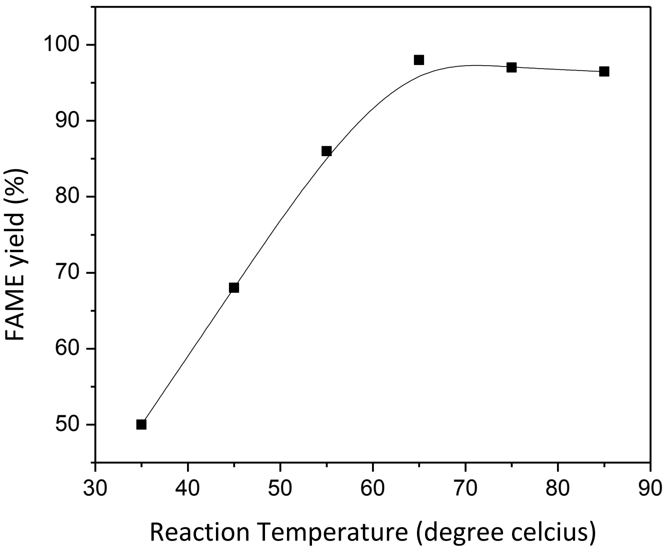


Fig.12. Effect of reaction temperature on FAME yield catalyst (reaction conditions: methanol/WCO molar ratio, 9:1; catalyst amount, 5 wt% with respect to oil and reaction duration, 1.5 hours).

Thus, a 9:1 methanol to oil molar ratio at 65 °C in the presence of 5 wt% catalyst (with respect to oil), was found to be an optimum condition for the 7-Ni-Zn/CaO-550 catalyzed transesterification of waste cooking oil (WCO).

4.3.5 Effect of the Moisture Contents on the Catalytic Activity:

Presence of >0.1 wt% moisture contents in the reaction mixture was found to deactivate the homogeneous alkali and acid catalysts. Heterogeneous catalysts, due to the immobilized active sites, are expected to demonstrate the higher moisture resistance. To prove the moisture resistance of Ni-Zn/CaO catalyst, the transesterification reactions of waste cooking oil were performed by adding up to 6 wt% (water/oil) water in the reaction mixture. As shown in Fig.13, the catalyst was found to be effective for the transesterification of WCO, even in presence of 5 wt% moisture contents. A further increase in moisture contents (>5 wt%) in the reaction mixture, results in catalyst deactivation, which could be due to the reaction between water and catalyst support (CaO) to yield the conversion of stronger Lewis basic (-O-) sites into weaker Bronsted basic (-OH) sites (Zhang *et al*., 2010).

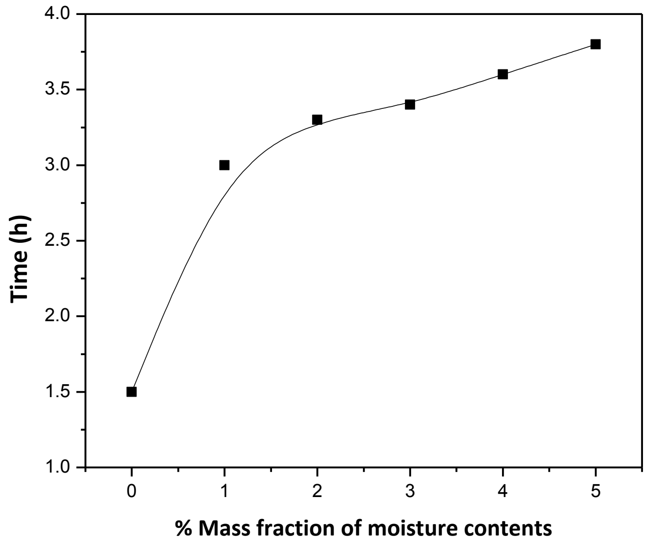


Fig.13. Effect of the moisture contents on the activity of Ni-Zn/CaO catalyst (reaction conditions: methanol/WCO molar ratio, 9:1; catalyst amount, 5 wt% with respect to oil; temperature, 65 °C; and reaction duration, 1.5 hours).

4.3.6 Reusability Study:

The reusability of the heterogeneous catalyst is an important advantage over the homogeneous catalyst because it could reduce the overall processing cost of the reaction. To test the reusability of 7-Ni-Zn/CaO, transesterification of the WCO was performed with methanol under optimized reaction conditions. After the completion of the reaction, Ni-Zn/CaO was recovered from the reaction mixture by filtration, washed with hexane, and calcined at 550 °C. The catalyst hence recovered and regenerated was employed for 3 successive catalytic cycles under the same experimental and regeneration methods. As shown in Fig.14, the reused catalyst was also found to yield >98% FAME yield in two successive catalytic runs. However, after the third cycle, partial conversion was achieved even after 8 hrs. of reaction period.

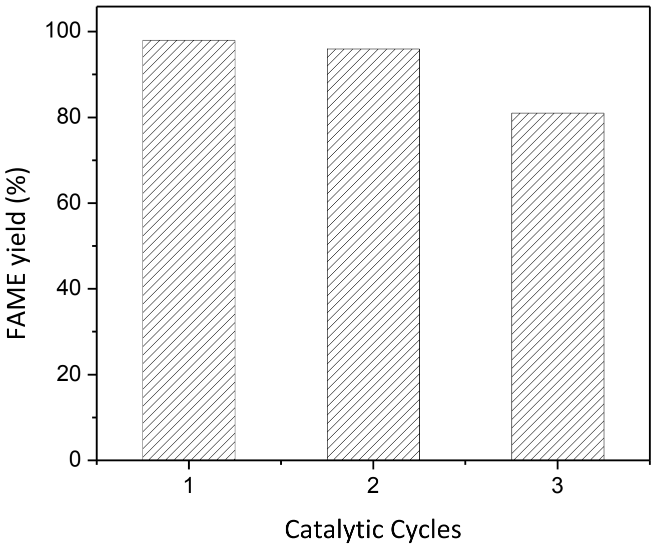


Fig.14. Reusability studies of 7–Ni-Zn/CaO–550 catalyst transesterification of WCO (reaction conditions: methanol/WCO molar ratio, 9:1; catalyst amount, 5 wt% with respect to oil; temperature, 65 °C; and reaction duration, 1.5 hours).

The gradual loss of the catalytic activity could be due to (i) the blockage of active sites because of the adsorbed organic molecule, and/or (ii) the partial leaching of the active species from the catalyst.

Fig.15 (a) and (b) shows the FT-IR spectra of fresh and reused 7-Ni-Zn/CaO. As shown in Fig.15 (a), a broad and sharp peak at 1427 cm^{-1} and 875 cm^{-1} are the peaks characteristic to CaO. The transmittance band observed at 3638 cm^{-1} is for $Ni(OH)_2$, The transmittance band at 3638 cm^{-1} and 870 cm^{-1} are of OH stretching vibrations and vibration of water absorbed on the surface respectively. However, in Fig.15 (b) the absence of the peak at 3638 cm^{-1} ($Ca(OH)_2$ and CaO), and presence of the broad band at 1427 cm^{-1} along with 870 cm^{-1} peak, indicated that calcium is mainly in the form of $CaCO_3$. New peaks corresponding to 2875-2975 cm^{-1} are the characteristic peaks of triglyceride oil spectrums which appear as a result of $–CH_2$ symmetric and asymmetric stretching vibrations.

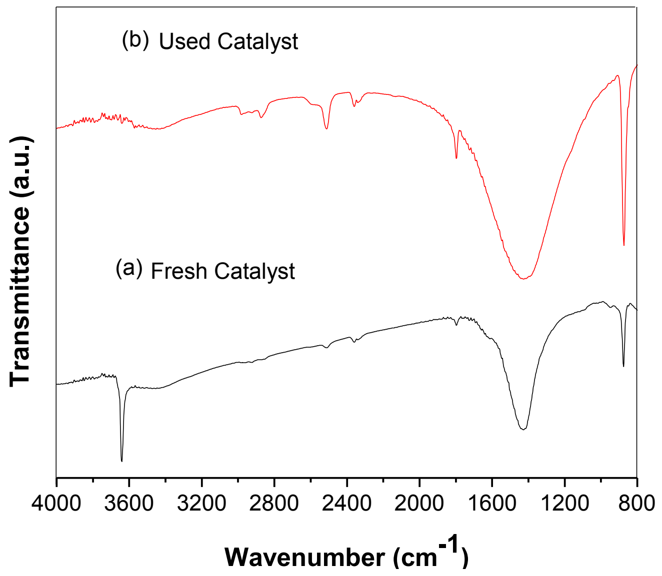


Fig.15. Comparison of FTIR spectra of (a) fresh and (b) used catalyst.

4.4 KINETIC MODELLING

4.4.1 LANGMUIR-HINSHELWOOD-HOUGEN-WATSON (LHHW) MODEL:

According to the product distribution, the system can be defined by the following reaction:

$$\text{Trigylceride + Alcohol} \xrightleftharpoons{\text{Catalyst}} \text{Biodiesel + Glycerol}$$

For the rate of disappearance of oil, Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was used to fit the kinetic data.

The rate expressions using LHHW model with surface reactions as the rate controlling step are,

I. For Dual Site Mechanism:

$$\mathbf{\underset{\cdot S}{M} + \underset{\cdot S}{O} \xrightarrow{k_1} B + G}$$

$-r_{oil} = dX_{oil}/d\tau = (k_1K_MK_OC_MC_O)/Z^2$ (1)

where $Z = (1+K_MC_M+K_OC_O)$ (2)

II. For Single Site Mechanism:

$$\mathbf{M + \underset{\cdot S}{O} \xrightarrow{k_1} B + G}$$

$-r_{oil} = dX_{oil}/d\tau = (k_1K_OC_MC_O)/Z^2$ (3)

where $Z = (1+K_OC_O)$ (4)

III. For Stoichiometry Model:

$$\mathbf{M + O \xrightarrow{k_1} B + G}$$

$-r_{oil} = dX_{oil}/d\tau = k_1C_MC_O$ (5)

where, k_1 is rate constant of reaction, K_M, K_O are adsorption coefficients of methanol and oil and C_M, C_O are concentrations of methanol and oil respectively.

A non-linear regression was used for model parameter estimation. The optimum values of parameters were predictable by minimizing the objective function given by equation.

$$f = \sum_{i=1}^{n}[(\,Rate\ predicted\,)i - (\,Rate\ observed)i]^2$$

4.4.2 Model Selection:

The experimental data was fitted in LHHW model to evaluate various rate constants of hypothetical reaction scheme. The terms for transesterification using LHHW approach with surface reaction as a rate controlling step and dual site (both reactant adsorbed on catalyst) mechanism were found to fit the kinetic data significantly better than the other (single and stoichiometry) models.

The kinetic rate constant and adsorption coefficients evaluated by nonlinear regression are given in Table 3 for dual site model with the estimated error of 2.04×10^{-8}. The experimental and the predicted rates for this model, at different temperatures, are plotted in Fig.16. The plots show a good correlation between the experimental and predicted rates having R^2 value of 0.94.

Table 3: Kinetic rate constants and adsorption coefficients for dual site

Temperature (K) / Kinetic Parameters	308	318	328	338
k_1 (sec^{-1})	**0.013**	**0.02**	**0.03**	**0.057**
K_M ($mole^{-1}$)	**21.45**	**10.55**	**9.52**	**8.45**
K_O ($mole^{-1}$)	**23.42**	**88.10**	**131.64**	**235.05**

where k_1 is rate constant and K_M and K_O are adsorption coefficients of methanol and oil respectively.

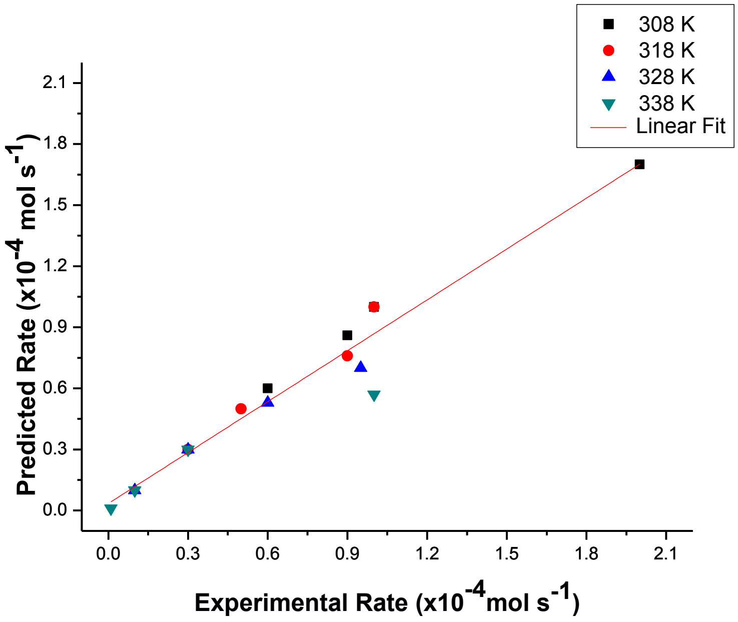


Fig.16. Experimental versus predicted rate

The kinetic constants resulting from equation (1), was used to found the activation energy, using Arrhenius equation (6).

$$\ln k = \ln A - E_a / RT \qquad (6)$$

Activation energy for transesterification reaction was estimated to be 43.15 kJ/mol and pre-exponential factor was 2.4×10^5 min^{-1}. An apparent activation energy value of 43.84 kJ/mol was calculated for transesterification reaction of triglyceride with methanol through pseudo first order equation. Another important thermodynamic parameters like enthalpy and entropy of adsorption were calculated using equation (7). The adsorption equilibrium constants are plotted in Fig.17 which shows a satisfactory trend. The values of enthalpy and entropy change are reported in Table 4.

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (7)$$

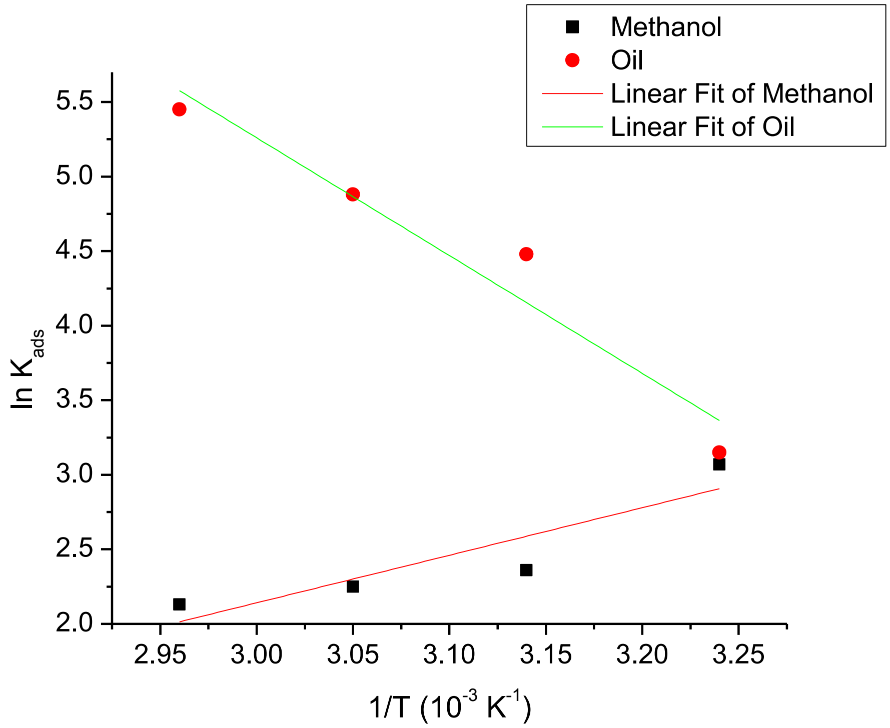


Fig.17. Arrhenius plot for adsorption equilibrium constants

Table 4: Thermodynamic adsorption parameters for methanol and waste cooking oil (WCO)

Reactants	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol K)
Methanol	**-12.164**	**-28.326**
WCO	**65.685**	**240.791**

CHAPTER 5

CONCLUSION

CONCLUSION

The catalyst, 7-Ni-Zn/CaO-550, has been prepared by a wet chemical method in nano crystalline 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 test. The Ni-Zn/CaO nano catalyst 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, 9:1; catalyst concentration, 5 wt% with respect to oil; reaction temperature, 65 ° C; and reaction duration of 1.5 hours, to achieve >98% FAME yield. Under optimized reaction conditions, Ni-Zn/CaO catalyzed transesterification of waste cooking oil (WCO) was found to follow dual site kinetic mechanism. The pre-exponential factor and activation energy for the same reaction were found to be 2.4×10^{5} min^{-1} (at 65 °C) and 43.15 kJ mol^{-1}, respectively. Further, the catalyst could be employed for 3 catalytic cycles without significant loss in activity.

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