PREPARATION OF ZINC OXIDE SUPPORTED HETEROGENOUS CATALYST FOR THE TRANSESTERIFICATION OF COTTON SEED OIL

A

Thesis Submitted

In partial fulfilment of the requirements for the

Degree of

Master of Science in Chemistry

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June 2010

ACKNOWLEDGEMENT

I thank God almighty for showering his blessings on me.

I wish to thank Dr. Susheel Mittal for allotting me the field of my interest for this thesis work. I want to pay my gratitude to my thesis supervisor Dr.Amjad Ali for his continuous guidance and support throughout these 6 months. I also want to thank Ph.D. scholars Mr.Dinesh Kumar, Mr.Vishal, Ms.Mandeep Kaur and my labmate Navjot for their continuous support and help.

I am highly obliged to the laboratory staff Chander Sir and Praveen Sir for their timely help in every possible way.

I thank my parents and my sister for always being there for me and motivating me throughout.

Priyanka

Place: Patiala

Date: 15 July 2010

CANDIDATE'S DECLARATION

I here by declare that the work being presented in the thesis entitled **"Preparation of zinc oxide supported heterogenous catalyst for the transesterification of cotton seed oil",** in partial fulfilment of the requirement for the award of degree of Master of Science in chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January 2010 to June 2010 under the supervision of Dr. Amjad Ali, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree.

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

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This is to certify that the thesis "**Preparation of zinc oxide supported heterogenous catalyst for the transesterification of cotton seed oil**" being submitted by Ms.Priyanka in partial fulfilment of requirements for the award of degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University Patiala, is a bonifide work carried out under the supervision of Dr. Amjad Ali and that no part of this thesis has been submitted for the award of any other degree.

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ABSTRACT

In the present thesis, a series of metal ions (Na, Co, Ni, Cu) were impregnated in ZnO and MgO supports and investigated for their catalytic activities towards transesterification of cotton seed oil. Sodium ion impregnated ZnO catalyst was found to show the maximum catalytic activity for cotton seed oil. The catalysts were prepared using wet impregnation method followed by calcinations, and prepared catalysts were used for the transesterification of cottonseed oil with methanol to produce biodiesel. The catalyst was characterized by using powder X-ray diffraction (XRD), Scanning Electron Microscopic (SEM) studies and their basic strengths were measured by Hammett Indicators. The catalytic activities of the prepared catalysts for the transesterification reaction of cotton seed oil were found to be dependent on the amount of Na ion impregnated in ZnO support and calcination temperature. The catalyst with 5 wt-% Na ion impregnated in ZnO support and calcined at 400 °C was found to show the maximum catalytic activity and used to optimize the reaction conditions for the transesterification reaction of cotton seed oil. The complete transesterification of the same with methanol (18:1 molar ratio, MeOH:oil) was observed in 1 h of reaction period at 65 °C.

CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 INTRODUCTION

Depleting resources of fossil fuel due to heavy consumption, global warming and environmental pollution are the diverse reasons for the search of alternate and renewable energy resources, such as biodiesel, in recent past. Biodiesel has several advantages over conventional diesel fuel, such as, derived from renewable resources, free from aromatic compounds, causes lower emissions of carbon monoxide, particulate matters, sulphur compounds and greenhouse gases due to its closed carbon dioxide cycle[1]. The word biodiesel comes from two terms bio + diesel. Bio refers to biological in origin and diesel refers to the fuel. Biodiesel is chemically a fatty acid methyl ester (FAME) formed by transesterification of triglycerides found in animal fat or vegetable oil with short carbon chain alcohols in the presence of some catalyst.

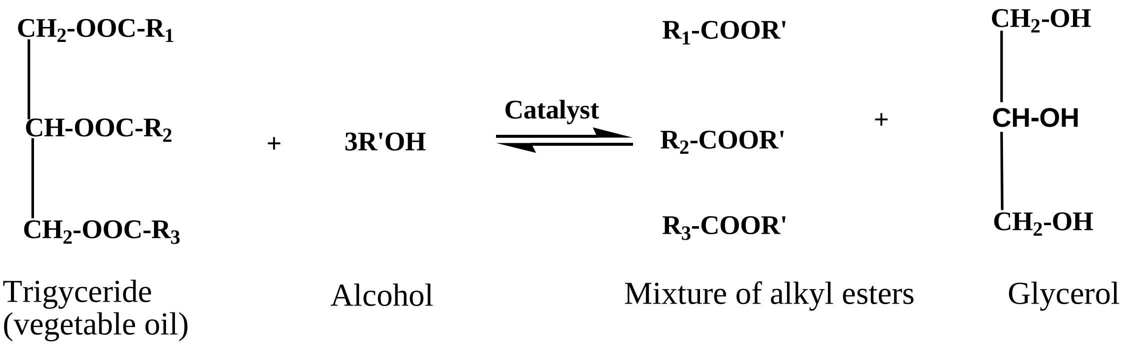


Figure 1. Transesterification reaction of vegetable oil/fat in the presence of methanol and catalyst.

Power required for agriculture and transportation sector is mainly based on diesel fuel[2]. The non renewable energy sources have led to global warming, environmental pollution, ozone depletion and climate change and have caused a great concern for the coming generations. Steps must be taken in this regard, to meet the never ending demands as well as to minimise the use of pollution causing agents. So, an alternative fuel is being searched that ensures good correlation with energy conservation and management, efficiency, sustainable development and environmental preservation. Biological fuels such as alcohol, vegetable oils, biomass, biogas, compressed natural gas (CNG), liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are under study as alternatives to conventional diesel fuel[3]. However, vegetable oils are a good option[2].

Though neat vegetable oils have energy density, heat of vapourisation, cetane number and air fuel molar ratio comparable to diesel fuel[2], but these cannot be used directly as fuels because of their high viscosity. This is due to their long chain structure, low volatility and tendency of polymerisation[4]. There is improper combustion and poor atomisation of fuel particles and carbon deposition on the injector and valve seats which leads to engine fouling[5]. So, we have tried to generate fuel similar in properties to that of diesel fuels but that are much greener and ecofriendly[6].

Biodiesel formed by transesterification reaction of vegetable oil leads to reduced amount of CO_2 emissions, NO_x, SO_x, particulate matter and green house gases[7]. It is easily biodegradable, ecofriendly and non toxic fuel with negligible sulphur content[6,8].

Biodiesel is environmentally friendly as CO_2 emitted by petroleum diesel was fixed from the atmosphere during earth formative years whereas CO_2 emitted by biodiesel is continuously fixed by plants and can be recycled by next generation crops. Thus, carbon cycle time for biodiesel is too small as compared to millions of years for petroleum diesel[2]. This renewable fuel is being used to run diesel engine cars, buses, trucks, construction equipment, boats and generators[9] .

1.2 LITERATURE SURVEY

Biodiesel is a fatty acid methyl ester (FAME) formed from renewable sources with short carbon chain alcohols in the presence of some catalyst. Vegetable oil was tested for the first time as fuel by Rudolf Diesel hundred years before. However in 1930s and 1940s these were only used in times of emergency. But due to increasing crude oil prices and limited fossil fuel resources and environmental concerns, vegetable oils and fats are being studied on a large scale now a days. Though there are various methods for the production of biodiesel such as dilution, microemulsions, pyrolysis, catalytic cracking and transesterification; transesterifying vegetable oils with short carbon chain alcohols using heterogenous catalyst is the best option[10].

Pyrolysis refer to chemical change undergone by a substance on application of thermal energy in the presence of air or nitrogen. Various vegetable oils give different products on thermal treatment. Though pyrolysed substance have low viscosity, high cetane number, acceptable amounts of sulphur and water but they are not acceptable in terms of ash, pour point and carbon residues[11].

Microemulsions with short carbon chain alcohols can solve the problem of high viscosity, cetane number, sulphur and ash content but problems of irregular injector needle sticking, heavy carbon deposits and incomplete combustion were encountered[11].

Biodiesel can be best produced by the transesterification process. Transesterification is the displacement of alcohol from an ester by another alcohol to form FAME. The process of transesterification is affected by the mode of reaction, molar ratio of alcohol to oil, type of alcohol, nature and amount of catalysts, reaction time, and temperature[3]. Transesterification reaction requires stoichiometrically three moles of methanol for one mole of triglyceride but due to reversible nature of the reaction, a higher molar ratio is used to obtain higher ester yields[5]. Both methanol and ethanol can be used for this process. The physical and chemical properties of both ethyl and methyl esters were comparable. However, viscosity of ethyl esters was slightly higher than that of methyl esters. Cold flow properties of ethyl esters were better than those of methyl esters. It is observed that methyl esters produced slightly higher power than ethyl esters. Exhaust emissions of both esters were almost identical[12]. Methanol is most commonly used due to its physical and chemical properties. However it is toxic. So, ethanol is being preferred as it is renewable and less toxic. However, in this case the products are less stable and less greener[8]. Glycerol obtained as by product is recovered for use in pharmaceutical, cosmetics, food and plastic industries[13].

Various raw materials can be used for the production of biodiesel. Both edible and non edible oils such as coconut oil, Jatropha curcas, castor oil, cotton seed oil, mahua and Karanj oil can be used[9]. Oil from algae, bacteria and fungi; and terpenes, latexes and grease are also known to be used[14]. Rice bran, a coproduct of rice milling can also be used[15]. Greases form the best renewable source for biodiesel production. Greases are composed of triglycerides, diglycerides, monoglycerides, and free fatty acids (8–40 wt-%). A grease containing (8–12 wt-% FFA) is known as a yellow grease, and a grease containing (>35 wt-% FFA) is known as a brown grease. Greases are pretreated to reduce the FFA content. They are reacted with diarylammonium catalysts to esterify FFA and are then transesterified[16].

Depending on the availability of the oil or fat different countries utilize different feed stock for biodiesel production[9].

Table 1. Feed stock for biodiesel production in different countries.

COUNTRY	SOURCE OF BIODIESEL
USA	Soyabean oil
China	Guang pi oil
Europe	Rapeseed oil and Sunflower oil
Spain	Linseed and Olive oil
Indonesia	Palm oil
Australia	Animal fat, beef tallow and rapeseed oil
Canada	Soybean oil / animal fat
India	Jatropha oil

Fatty acids vary in carbon chain length and in the number of unsaturated bonds. The fatty acids composition of few vegetable oils is given in Table 2[17].

Table 2. Fatty Acid Composition (wt-%) of various Vegetable Oils.

FATTY ACID	SOYBEAN	COTTONSEED	PALM	COCONUT
Lauric	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	19.2
Palmitic	10.2	20.1	42.8	9.8
Stearic	3.7	2.6	4.5	3.0
Oleic	22.8	19.2	40.5	6.9
Linoleic	53.7	55.2	10.1	2.2
Linolenic	8.6	0.6	0.2	0.0

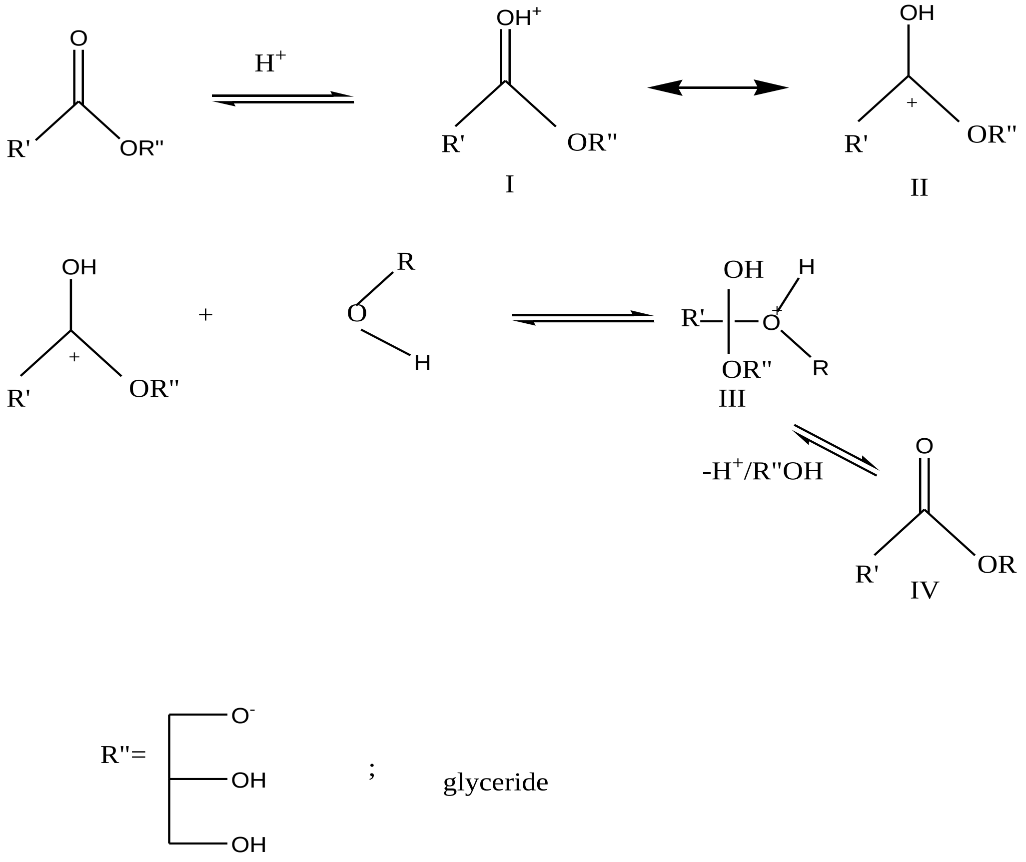
The most advanced work with sunfower oil occurred in South Africa because of the oil embargo. The first International Conference on Plant and Vegetable Oils as fuels was held in Fargo, North Dakota in August 1982[17].

Transesterification reaction of vegetable oils was performed many years before the diesel engine came into picture in 1853 by E. Duffy and J. Patrick[9]. Biodiesel is produced by the base catalysed process[1], acid catalysed process[18], supercritical process[19] and enzymatic process[20]. A catalyst is usually used to improve the reaction rate and yield.

In **enzyme-catalyzed transesterification methods**, oils with high acid content can be used and glycerol formed as the by product can be recovered easily. Also, there are no side reactions produced in this case. But, however, high cost of enzymes discourages its use on commercial scale[21]. Both **acid and base catalysts** can be used for transesterification reaction.

ACID CATALYSED TRANSESTERIFICATION:

Sulphuric, phosphoric, hydrochloric or organic sulfonic acid can be used as acid catalysts. Methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4 with an alcohol/oil molar ratio of 30:1 at 65 ºC , takes 50 h for complete conversion of the vegetable oil (>99%)[3]. Al-Widyan et al performed transesterification of used palm oil under various conditions using different concentrations of HCl, H_2SO_4, and excess ethanol. It was found that at higher catalyst concentrations (1.5–2.25 M), H_2SO_4 offered better conversion levels than HCl at a catalyst concentration of 2.25 M[22]. Superacid sulfated titania catalyst, TiO_2/SO_4 (TS-series), prepared via the sol–gel technique can be used for transesterification of soybean and castor oils at 120 ºC, for 60 min (40% and 25%, respectively)[23]. Heteropolyacids can be better used because of geater proton mobility, and existence in solid form so as to mediate the transesterification of liquid oils. The multiple acidic protons can continue catalysis when bound to a glycerol molecule even in the presence of water. But, they can not be used in the presence of > 1% water.



R' = carbon chain of fatty acid

R = alkyl group of alcohol

Figure 2. Mechanism of acid catalysed transesterification of vegetable oils.

However, acid catalysts have lower activity even at high temperature and oil: methanol molar ratio of 1:30 - 150. So, acid catalysts are used when vegetable oils/fats have higher FFA and water content[24].

BASE CATALYSED TRANSESTERIFICATION:

Base catalysed reactions are sensitive to moisture and free fatty acid content. Anhydrous conditions must be used so as to prevent the saponification reaction that leads to unnecessary utilization of the catalyst and separation problems[21]. However, some of the soap formed is used to neutralise the free fatty acid content in the feedstock[24], acts as a phase transfer catalyst and assist mixing of the reactants, thus increasing the surface area for the reaction by formation of tiny droplets.

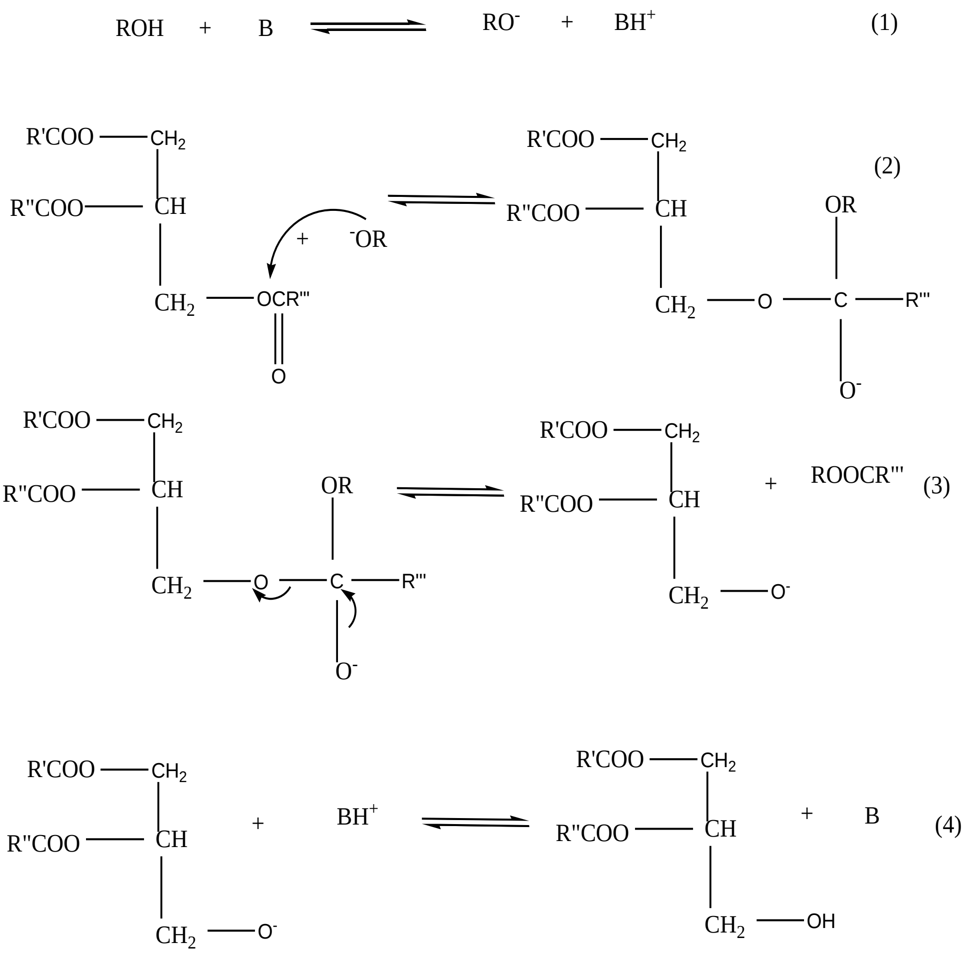


Figure 3. Mechanism of base catalysed transesterification of vegetable oils.

Homogenous base catalysts such as NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide are being preferred as compared to acid catalysts due to their higher activity, easy availability and cost effectiveness[25]. Mostly KOH is utilized, as, at the end of reaction, the mixture can be neutralized with phosphoric acid to afford potassium phosphate, which is a fertilizer.

Karanja oil was transesterified to biodiesel under the reaction conditions of 1 atm pressure, 68-70 ºC temperature, molar ratio of methanol:oil of 8-10, 1.5 wt-% KOH catalyst in a reaction time of 30-40 min[26]. The activity and efficiency of nonionic bases as catalysts in homogeneous media has also been studied.

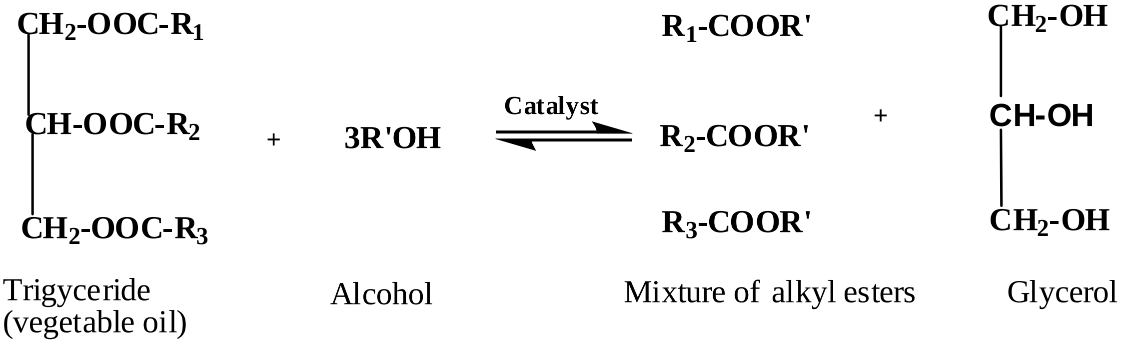
Some guanidines can be used as homogenous base catalysts. 1,5,7-triazabicyclo[4.4.0]dec-5-ene(TBD) produces more than 90% of methyl esters after 1 h with only 1 mol% in the reaction mixture. Yields obtained with TBD were close to those observed with NaOH with no by-products such as soaps[3]. Metal complexes of the type M(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$, where M= Sn, Zn, Pb, and Hg, have been used for soybean oil methanolysis under homogeneous conditions. Sn and Zn complexes showed great activities with yields of up to 90% and 40%, respectively, in 3 h, using a molar ratio of 400:100:1 (methanol:oil:catalyst), without emulsion formation[3]. Recently, liquid amine-based catalysts were also studied as catalysts. Tertramethylammonium hydroxide (TMAH) (as 25% in methanol) yielded 98% methyl esters at 65 ºC in 90 min[3].

Transesterification reaction of waste cooking oil (WCO) is performed via two step catalysed process. The first step involves acid catalysed esterification to reduce the free fatty acid contents (FFAs) and the second step involves transesterification using basic catalyst. Similar two step process was reported in which ferric sulphate was used in the first step for esterification and KOH in the second step for transesterification for WCO. Thus, with 2 wt-% catalyst amount with methanol: triglyceride molar ratio of 10:1 and reaction time of 4 h; conversion of FFA was 97.20%. This upon transesterification with KOH resulted in 97.02% yield after 1 h of reaction period[27].

STEP 1

$$RCOOH + CH_3OH \xrightarrow{Fe_2(SO_4)_3} RCOOCH_3 + H_2O$$

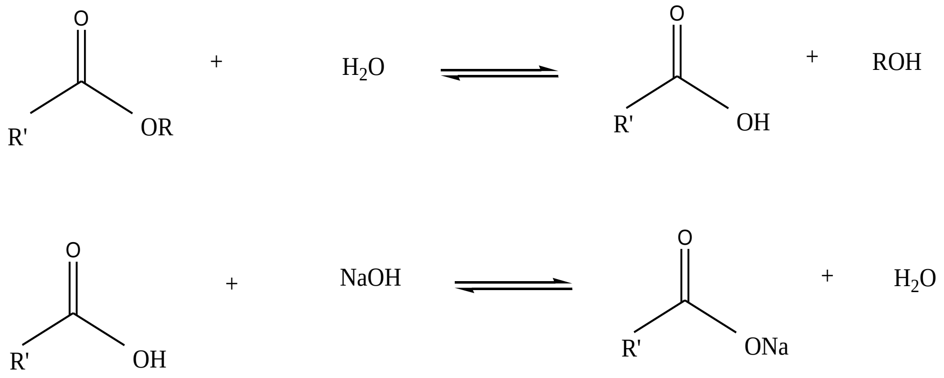
STEP 2



$$\begin{array}{l} CH_2\text{-}OOC\text{-}R_1 \\ CH\text{-}OOC\text{-}R_2 \\ CH_2\text{-}OOC\text{-}R_3 \end{array} + 3R'OH \xrightleftharpoons{\text{Catalyst}} \begin{array}{l} R_1\text{-}COOR' \\ R_2\text{-}COOR' \\ R_3\text{-}COOR' \end{array} + \begin{array}{l} CH_2\text{-}OH \\ CH\text{-}OH \\ CH_2\text{-}OH \end{array}$$

Figure 4. Two step catalysed process involving simultaneous esterification and transesterification reaction.

Homogenous base catalyzed transesterification yielded complete conversion in very short duration of reaction, however, same catalyst leads to the formation of soap if FFA and moisture contents in feedstock is > 0.5 wt-%. This leads to the deactivation of catalyst and causes the problem of basic catalyst recovery and glycerol and required excessive alcohol separation that adds to the production cost[24]. So, homogenous catalysts are being replaced by heterogenous catalysts in which the catalyst can be easily removed and can even be reused for further reactions.



R' = carbon chain of the fatty acid

R= alkyl group of alcohol

Figure 5. Saponification reaction of produced fatty acid alkyl esters

Commercial hydrotalcite, $CaCO_3$ rock, Na/NaOH/γ-Al_2O_3, modified zeolite and Li/CaO have been determined to be efficient for the transesterification reaction[24]; however, as they are quite expensive and complicated to prepare, they have limited industrial application. So, cheap heterogenous catalysts are being worked upon to reduce the production costs. Heterogenous catalyst results in the formation of uncontaminated products, is recyclable, has low sensitivity toward FFAs and moisture content, and does not corrode the reaction vessel[28,29].

The nanocrystalline calcium oxides with a crystal size of 20 nm and specific surface area of 90 m^2/g give 100% conversion of soybean oil at room temperature after 12 h[28].

Catalytic activity of calcium oxide (CaO) can be accelerated for transesterification of plant oil. CaO was activated by pretreatment with methanol. The optimal reaction conditions were 0.1 g CaO, 3.9 g methanol, 15 g rapeseed oil, and 1.5 h activation time at room temperature that provided Me ester in approx. 90% yield within a reaction time of 3 h at 60 ºC. The activation mechanism involved conversion of CaO into $Ca(OCH_3)_2$ that acts as an initiating reagent for the transesterification reaction and produces glycerine as a byproduct. Subsequently, a calcium-glycerin complex functions as the main catalyst and accelerates the transesterification reaction[30]. Nanocrystalline Li ion impregnated CaO has been used for transesterification of used cotton seed oil under optimum conditions of 1:12 molar ratio of oil:methanol and 5 wt-% catalyst at 65 ºC to attain a yield of >98% in 45 min[1]. 14 wt-% of CaO supported on SBA-15 was the most active catalyst for the reaction of ethyl butyrate with methanol, reaching conversion as high as 95% with sunflower oil (after 5 h of reaction) and 65% (after 1 h) for castor oil[31]. The catalyst modified from dolomite calcined at 600 ºC and 700 ºC, followed by the precipitation from $Ca(NO_3)_2$ and the subsequent calcination at 800 ºC, exhibited the most active catalyst for the transesterification of palm kernel oil, giving the methyl ester content as high as 99.9% under the suitable reaction conditions of the methanol/oil molar ratio of 15, 10 wt-%(catalyst/oil), and reaction time of 3 h[32]. The CaO and $MgO\text{-}Al_2O_3$ have high catalytic activity for transesterification, and the yield of Me esters reached over 90% under the conditions of 230 ºC, methanol/oil mole ratio of 12, and 2 wt-% (catalyst/oil) after reaction of 3 h[33].

Good results in transesterification of soybean oil were obtained using sodium aluminate as catalyst. When the transesterification reaction was carried out at reflux of methanol (65 °C), with a 12:1 molar ratio of methanol to soybean oil and a catalyst amount of 1.5 wt-%, the conversion of soybean oil was 93.9% after a reaction period of 50 min[34]. Palm kernel oil (PKO) and coconut oil (CCO) were transesterified over $Ca(NO_3)_2/Al_2O_3$ with methanol/oil molar ratio of 65, temperature of 60 ºC and reaction time of 3 h, with 10 and 15-20% (w/w) catalyst to oil ratio for PKO and CCO, resp[35].

Noiroj et al recently reported the comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production. The 25 wt-% KOH/Al_2O_3 and 10 wt-% KOH/NaY catalysts are suggested to be the best composition because of their biodiesel yield of 91.07% at temperatures below 70 ºC within 2-3 h at a 1:15 molar ratio of palm oil to methanol and a catalyst amount of 3-6 wt-%[36].

Sodium molybdate (Na_2MoO_4) used as heterogeneous catalyst for methanolysis of soybean oil rendered transesterification under relatively mild conditions, requiring low temperatures, short times, and normal pressure with yields higher than 95%. The catalyst was easily recovered and recyclable for another catalytic reaction with similar activity[37]. Magnesium-lanthanum-mixed oxide catalysts with different Mg/La ratios prepared by coprecipitation at a constant pH method can be used for the transesterification of oils containing both water and free fatty acids. The catalyst can be easily recovered and reused with consistent activity[38]. The transesterification of rice bran oil with methanol was done with dibutyl tin dilaurate ($(C_4H_9)_2Sn(C_{12}H_{23}O_2)_2$), known commercially as DBTDL with a yield of 68.9% in 4 h using molar ratio 400:100:1 (methanol:oil:catalyst)[15].

Pure ZnO with high % purity can also be used for transesterification reaction of crude palm kernel oil and crude coconut oil. Under the experimental conditions of methanol: oil molar ratio of 6:1, 3% catalyst by weight of oil, pressure at 50 bars under N_2 atmosphere, 200 ºC temperature, and the 350 rpm stirrer; methyl ester yield was 86.1% for palm kernel oil and 77.5% for coconut oil[39]. As, high temperature and pressure conditions are required for pure ZnO, so it was doped with certain metal ions so as to use mild reaction conditions and increase % yield. 15-KF/ZnO-600 for 5 hrs gives 87% conversion of soybean oil when refluxed for 9 hrs with molar ratio of methanol: oil of 10:1[26]. Zn/I_2, can act as heterogenous catalyst for the transesterification of soybean oil. 96 % conversion was obtained under optimum conditions with this catalyst[40]. 5-Li/ZnO resulted in a soybean oil conversion of 96.3% in 3 h using a 12:1 molar ratio of methanol to oil[24]. The transesterification of soybean oil to biodiesel using Ba–ZnO as a solid catalyst was studied. The Ba–ZnO sample with loading of 2.5 mmol/g Ba on ZnO and being calcined at 600 ºC for 5 h, was found to be the optimum catalyst, which could exhibit the highest basicity and the best catalytic activity for the reaction. When the transesterification reaction was carried out at reflux of methanol (65 ºC), with a 12:1 molar ratio of methanol: oil and a catalyst amount of 6 wt-%, the conversion of soybean oil was 95.8%[41]. ZnO loaded $Sr(NO_3)_2$ followed by calcination at 600 ºC for 5 h can be used for the transesterification under the optimum conditions of reflux temp of methanol (65 ºC), with a 12:1 molar ratio of methanol to soybean oil and a catalyst amount of 5 wt-%, to give a yield of 94.7%.

However, the used catalyst was significantly deactivated and could not be directly reused for transesterification[42]. Transesterification of palm kernel oil with methanol over mixed Ca and Zn oxides was investigated batchwise at 60 ºC and 1 atmospheric pressure. CaO-ZnO catalysts were prepared by co-precipitation of the corresponding mixed metal nitrate solution in the presence of a soluble carbonate salt at near neutral conditions. The combination of Ca and Zn reduced the calcination temperature required for decomposition of metal carbonate precipitates to active oxides. Under the optimum conditions at 60 ºC (catalyst amount = 10 weight%, methanol/oil molar ratio = 30, reaction time = 1 h), the ME content of >94% can be achieved over CaO-ZnO catalyst with the Ca/Zn ratio of 0.25. It can also be used for transesterification of palm, soybean, and sunflower oils[43]. Heterogeneous zinc and lanthanum mixed oxides in the ratio of 3:1 simultaneously catalyzed the oil transesterification and fatty acid esterification reactions, while minimizing oil and biodiesel hydrolysis. A high yield (96%) of FAME was obtained within 3 h even using unrefined or waste oils under a reaction temperature of 170- 220 ºC[44].

Different properties of biodiesel such as density, viscosity, saponification value, iodine value, flash point, aniline point/cetane number, calorific value, cloud point, pour point etc. are compared with that of the conventional diesel fuel[45]. Thus in biodiesel, physical properties have been modified to improve engine performance[11]. However the cost of biodiesel is the major problem encountered in its commercialisation. So, raw materials such as low quality cheap feedstock, heterogenous catalyst, reduced time period for transesterification reaction involving lesser consumption of energy and recovery of purified glycerol as the by product must be considered as the major criteria to lower the cost[14].

As esterified oil have higher cloud point, so a blend of 20-25% of esterified oil with petroleum based diesel is used commercially[46]. Thus, a diesel engine on operation with biodiesel reduces exhaust emissions, 20% in CO, 30% in HC, 40% in particulate matter (PM), and 50% in soot emission.

EXPERIMENTAL SECTION

2.1 MATERIALS AND METHODS

Virgin, used cooking oil and fat procured from local sources at Patiala were used for the experimental studies. Metal salts viz. $NaNO_3$, Na_2CO_3, $Co(NO_3)_3.6H_2O$, $Ni(NO_3)_2$, $CuSO_4.5H_2O$ and methanol (99.8%) were purchased from Merck, India. Silica gel of reagent grade quality, for thin layer chromatography (TLC), MgO and ZnO were obtained from s d fine Chem Limited and used as such without further purification. Hexane, ethyl acetate and acetic acid used for solvent system were purchased from Loba Chemie, India and methyl oleate (99%) used as a biodiesel standard was procured from Sigma-Aldrich.

Powder X-ray diffraction (XRD) data was collected on Panalytical's X'Pert Pro with Cu K α radiation. The samples were scanned in the range of $2\theta = 5\text{-}80^0$ at the scanning speed of 2°/min. XRD was used to determine the particle size and the type of crystal planes found in the catalyst. Field emission scanning electron microscopy (FESEM) was performed on FESEM JEOL JSM 6510LV JAPAN to collect the SEM images of the catalysts. Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of biodiesel and vegetable oil were recorded on a Bruker Avance-II (400 MHz) spectrophotometer. ^{1}HNMR was performed to calculate the % yield of ester formation[47,48]. Basic strength of the catalyst was determined using Hammett indicators: neutral red ($H\_=6.8$), bromthymol blue ($H\_=7.2$), phenolphthalein ($H\_=9.3$), Nile blue ($H\_=10.1$), tropaeolin-O ($H\_ = 11.1$), 2,4-dinitroaniline ($H\_ = 15.0$), and 4-nitroaniline ($H\_ = 18.4$).

2.2 CATALYST PREPARATION

Sodium impregnated ZnO catalyst for transesterification reactions were prepared by following the literature reported wet impregnation method[1] with slight modification. In a typical preparation (e.g., the preparation of 5-Na_2CO_3/ZnO-400), 10 g of zinc oxide was suspended in 100 mL of deionized water, and to this 10 mL aqueous solution containing 1.155 g of Na_2CO_3 was added. The resulted slurry was stirred for 3 h, then evaporated to dryness and heated at 100 °C for 24 h and calcined at varying temperatures for 8 h.

Similarly catalysts were prepared using various amount of sodium (ranging 3-9 wt-% of ZnO) at varying calcination temperatures (200-600 ºC). Similar procedure was adopted to prepare the catalyst with other metal ions, viz., $NaNO_3$, Na_2CO_3, $Co(NO_3)_3.6H_2O$, $Ni(NO_3)_2$ and $CuSO_4.5H_2O$ impregnated in MgO and ZnO supports. Catalysts so prepared were characterized by Hammett Indicator test, powder X-ray diffraction and SEM studies. The appropriate catalyst was worked upon further for transesterification process.

The catalysts prepared in such a manner were designated as XX-MA/ZnO-T, where XX represents the percentage of impregnation in ZnO; MA represent the impregnated metal salt and T represents calcination temperature in degree celcious, e.g., 5-Na_2CO_3/ZnO-400 represents ZnO catalyst formed by impregnation of 5 wt-% of Na^+ using Na_2CO_3 salt and calcined at 400 ºC.

2.3 TRANSESTERIFICATION OF FRESH COTTON SEED OIL

In a typical transesterification reaction, vegetable oil (Mol wt, 860) and methanol in 1:18 molar ratio and 10 wt-% (catalyst/vegetable oil) were taken in a two neck, 50 mL round-bottom flask equipped with a water-cooled condenser and reaction mixture was stirred till the completion of the reaction at 65 °C.

Figure 6. Transesterification Setup.

The progress of the reaction and primary characterization of the products were carried out by thin layer chromatographic (TLC) technique using hexane/ethylacetate/aceticacid (90:9:1) as the mobile phase and silica gel as the stationary phase.

Biodiesel shows a higher mobility than vegetable oil with the selected solvent system, and complete conversion of vegetable oil to biodiesel was supported by the disappearance of the spot on the TLC plate.

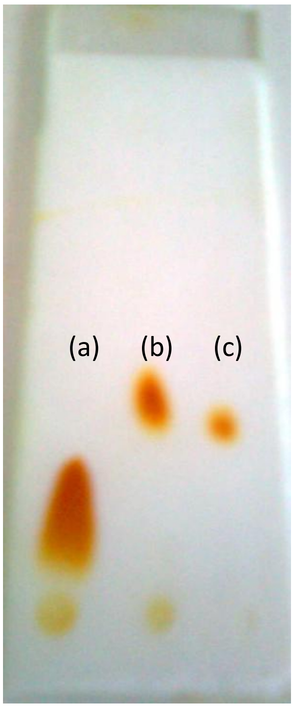


Figure 7. TLC analysis of (a) cotton seed oil, (b) biodiesel standard and (c) prepared cotton seed oil biodiesel**.**

Further biodiesel so produced was characterized by ^{1}H NMR spectroscopy, and the ^{1}H NMR technique was also used for the quantification of biodiesel using literature reported procedure[47,48] .

CHAPTER 3

RESULTS AND DISCUSSION

3.1 CATALYST CHARACTERISATION

Basic strength of the catalysts were determined with the help of Hammett Indicators and summarised in Table 3. The basic strength of 5-Na_2CO_3/ZnO-400 was found to be $9.3 < H\_ < 10.1$. Powder X-ray diffraction studies of various catalysts was performed and compared. XRD patterns of 5-$CuSO_4$/MgO-650, 5-$Co(NO_3)_3$/MgO-650, 5-$Ni(NO_3)_2$/MgO-650, 1-$Ni(NO_3)_2$/MgO-550 shows characteristic peaks at 2θ ~ 42.93 and 62.39 corresponding to the d-values of 2.10 and 1.48 respectively, of MgO, thus showing well dispersed phase on the surface of MgO. However, 1-$Ni(NO_3)_2$/MgO-100 shows characteristic peaks at 2θ ~ 18.82, 38.38 and 51.35 corresponding to d-values of 4.76, 2.35, 1.78 respectively, of $Mg(OH)_2$ as shown in Figure 8. Indexing was done on the basis of data obtained from JCPDS card no. 87-0653 and 86-0653.

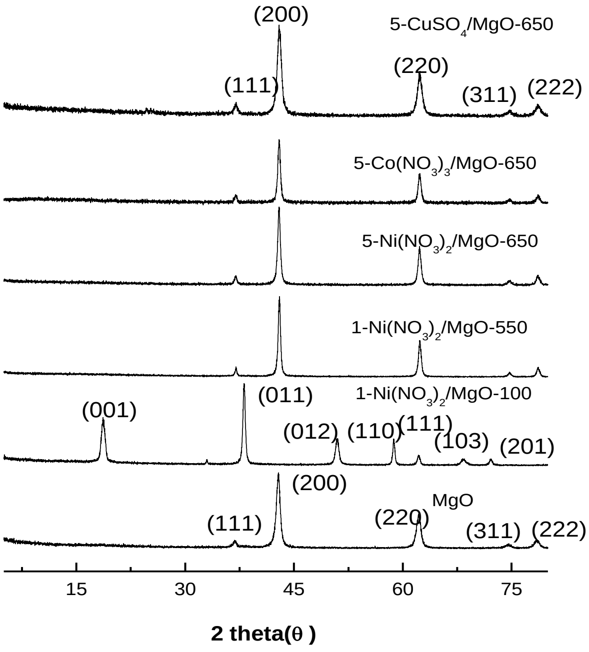


Figure 8. Comparison of powder XRD patterns of commercially available MgO and various metal salts impregnated in MgO .

XRD patterns of Na_2CO_3/ZnO-400 sample with varying amount of Na_2CO_3 (2-9 wt-% of Na^+ on ZnO) shows intense peaks at 2θ ~ 31.82, 34.48, 36.31, 47.59 corresponding to the d-values of 2.81, 2.60, 2.47, 1.90 respectively, of ZnO as shown in Figure 9. There are no new characteristic peaks indicating the well dispersion of Na_2CO_3 on ZnO.

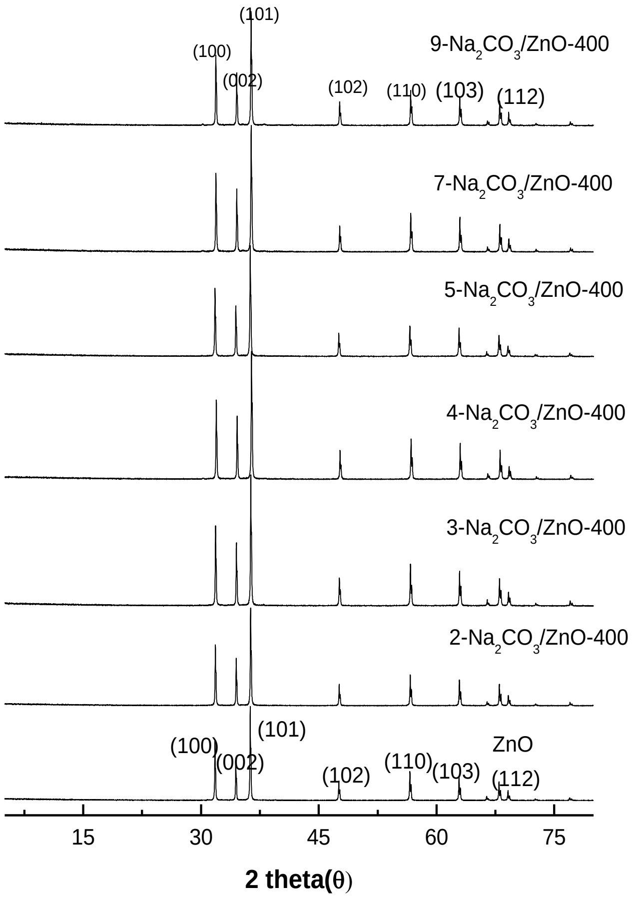


Figure 9. Comparison of powder XRD patterns of commercially available ZnO with 2-9 wt-% sodium loaded ZnO and calcined at 400 °C.

The characteristic peaks at 2θ ~ 36.26, 31.78, 34.43 corresponding to d- values of 2.47, 2.81, 2.60 respectively at different calcination temperatures in 5-Na_2CO_3/ZnO shows that they were similar to that of ZnO obtained commercially. This shows that there is no considerable distortion in the bulk structure of ZnO on impregnation of Na_2CO_3 and most likely sodium ions are occupying the interstitial space in the ZnO structure.

Indexing was done on the basis of data obtained from JCPDS card no. 89-1397 as shown in Figure 10 and diffraction pattern of the prepared catalyst were found to match with those of hexagonal packing.

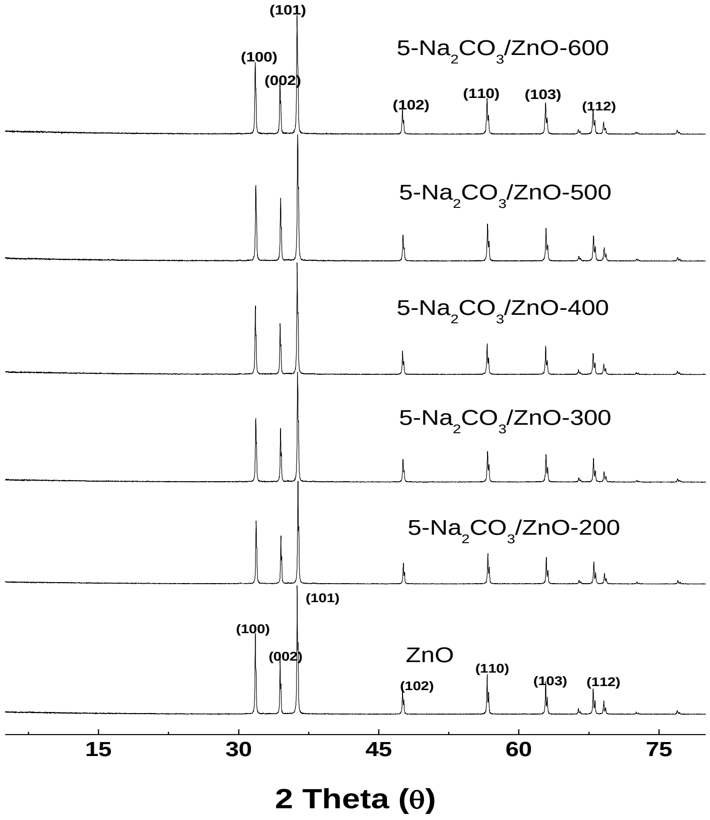


Figure 10. Comparison of powder XRD patterns of commercially available ZnO with 5-Na_2CO_3/ZnO at varying calcination temperatures.

Particle size of 5-$Na_2CO_3$was determined by Debye-Scherrer method[49] using powder XRD data as shown in Table 3.

Table 3. Basic Strength and Particle size of 5-Na_2CO_3/ZnO calcined at different temperatures**.**

S.No.	Catalyst Type	Basic Strength (H_-)	Particle Size(nm)
1	5-Na_2CO_3/ZnO -200	$9.3 < H_- < 10.1$	40.20
2	5-Na_2CO_3/ZnO -300	$9.3 < H_- < 10.1$	35.07
3	5-Na_2CO_3/ZnO -400	$9.3 < H_- < 10.1$	45.53
4	5-Na_2CO_3/ZnO -500	$9.3 < H_- < 10.1$	35.07
5	5-Na_2CO_3/ZnO -600	$9.3 < H_- < 10.1$	41.60

The surface morphology of the catalyst 5-Na_2CO_3/ZnO-400, have been investigated by scanning electron microscopy shown in Figure 11. The average size of the cuboid shaped catalyst particles by FESEM studies was found to be < 1µm. Particle size measurement by powder XRD studies revealed that these particles are the clusters of further smaller particles with average size of 45.53 nm.

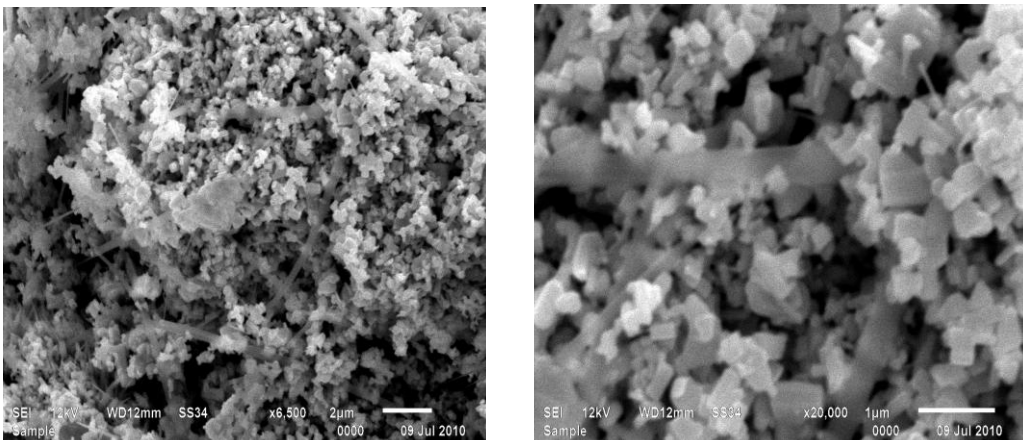


Figure 11. SEM images of 5-Na_2CO_3/ZnO-400

3.2 TRANSESTERIFICATION REACTIONS AND BIODIESEL CHARACTERISATION

Transesterification reactions of cotton seed oil with methanol (1:18 molar ratio) were performed in the presence of prepared catalysts (10 wt-% catalyst/oil) at 65 ºC. Prepared catalysts were used to carry out the transesterification reactions of cottonseed oil in order to determine the least reaction time for the completion of transesterification reaction. During the course of study, the following parameters have been varied (i) impregnated metal ions, (ii) impregnated sodium ion concentration, (iii) catalyst concentration, (iv) calcination temperature, (v) reaction temperature, (vi) oil/methanol molar ratio, (vii) variable feedstocks. Biodiesel produced in the transesterification reaction was quantified and characterised using ^{1}H NMR spectroscopy. The proton NMR spectrum of cottonseed oil shows a multiplet at 4.1 and 5.2 ppm due to the presence of glyceridic protons along with other hydrocarbon-proton peaks at their normal positions. The appearance of a new peak at 3.6 ppm due to -OCH_3 protons and disappearance of the glyceridic protons reveals the formation of biodiesel as shown in Figure 12.

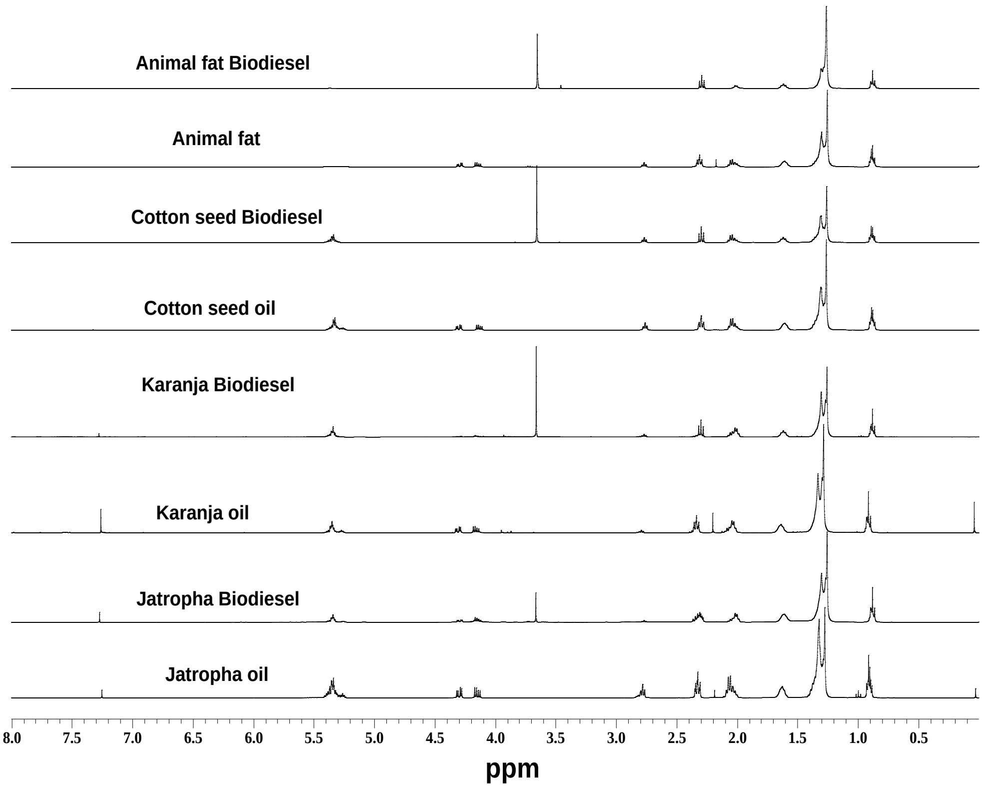


Figure 12. Comparison of the H^1 NMR spectra of oil/fat with that of corresponding biodiesel.

3.2.1. Effect of Different Metal Ions on Catalyst Activity

In order to study the effect of impregnated metal ions on the catalytic activity for the transesterification of cotton seed oil, a series of catalysts were prepared using MgO and ZnO supports. The results obtained were summarized in Table 4, and catalyst 5-Na_2CO_3/ZnO being better in activity than others was selected for further studies.

Table 4. Effect of impregnated metal salt on catalytic activity towards the transesterification of cotton seed oil.

S.No.	CATALYST	REACTION TIME (h)	CONVERSION*
1	1-$Ni(NO_3)_2$/MgO-550	2	No conversion
2	1-$Co(NO_3)_3.6H_2O$/MgO-650	8	Incomplete
3	5-$Ni(NO_3)_2$/MgO-650	9	No conversion
4	5-$Co(NO_3)_3.6H_2O$/MgO-650	20	No conversion
5	5-$CuSO_4.5H_2O$/MgO-650	14	No conversion
6	1-$Co(NO_3)_3.6H_2O$/ZnO-650	8	Incomplete
7	1-$Ni(NO_3)_2$/ZnO-650	12	Incomplete
8	3-$NaNO_3$/ZnO-650	6	No conversion
9	3-Na_2CO_3/ZnO-650	10	Complete
10	3-Na_2CO_3/ZnO-200	25	Incomplete
11	3-Na_2CO_3/ZnO-300	17	Incomplete
12	3-Na_2CO_3/ZnO-400	10	Complete
13	3-Na_2CO_3/ZnO-500	13	No conversion
14	4-Na_2CO_3/ZnO-400	3	Complete
15	5-Na_2CO_3/ZnO-400	1	Complete
16	7-Na_2CO_3/ZnO-400	7	Complete
17	9-Na_2CO_3/ZnO-400	10	Complete

***** on the basis of TLC

3.2.2 Effect of Impregnated Sodium Ion Concentration.

To determine the optimum amount of sodium ion impregnation in ZnO, a series of catalysts by varying the amount of sodium (ranging 3-9 wt-% of ZnO) were prepared. Transesterification of cottonseed oil was performed with methanol (1:18 molar ratio) at 65 ºC in the presence of prepared catalysts. The reaction time required for the complete transesterification was found to decrease from 10 h to 1 h as the amount of sodium ion in ZnO was increased from 3-5 wt-%. However, a further increase in Na ion concentration does not reduce the reaction time as shown in Figure 13, and hence, 5-Na_2CO_3/ZnO-400 catalyst was used for transesterification reactions to optimize other parameters for achieving the minimum time for the completion of the transesterification reaction.

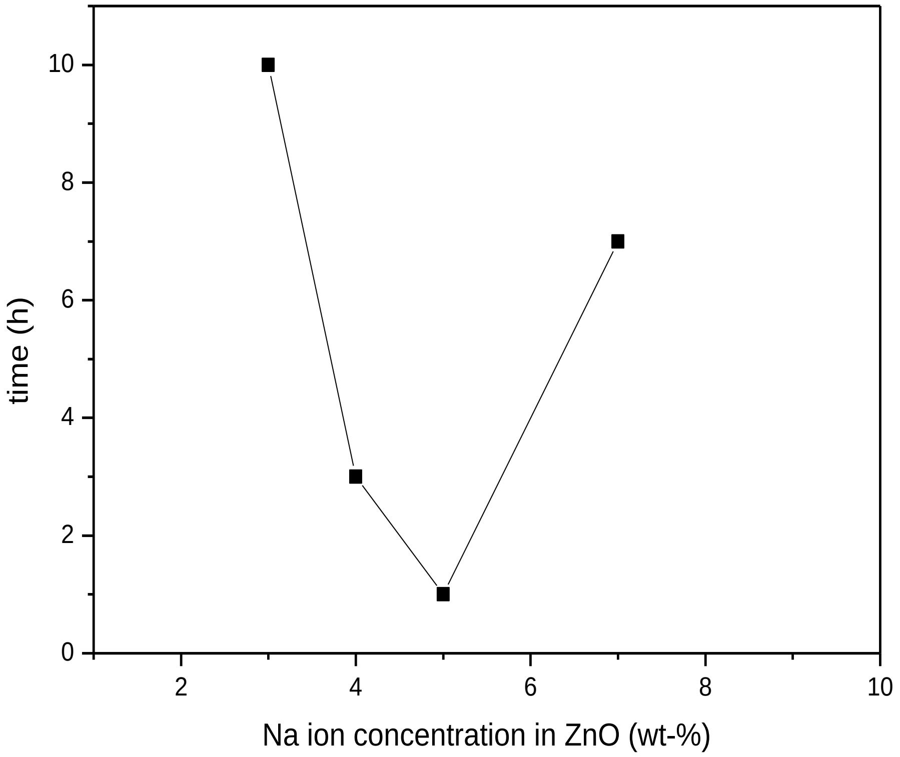


Figure 13. Effect of sodium ion concentration present in ZnO, on reaction time required for the complete transesterification of cottonseed oil.

3.2.3. Effect of Catalyst Concentration.

A series of transesterification reactions of cotton seed oil with methanol (1:18 molar ratio) at 65 ºC was performed in the presence of 5-Na_2CO_3/ZnO-400 by varying its concentration from 2.5-15 wt-% (catalyst/oil) in order to find the optimum catalyst concentration. Time required for the complete conversion of vegetable oil to biodiesel decreases from 1 h 45 min to 1 h as the catalyst concentration was increased from 2.5 to 10 wt-%. A further increase in the catalyst concentration does not reduce the reaction time significantly as shown in Figure 14. The transesterification reactions were further studied with a catalyst concentration of 10 wt-% of oil for optimization of the other parameters.

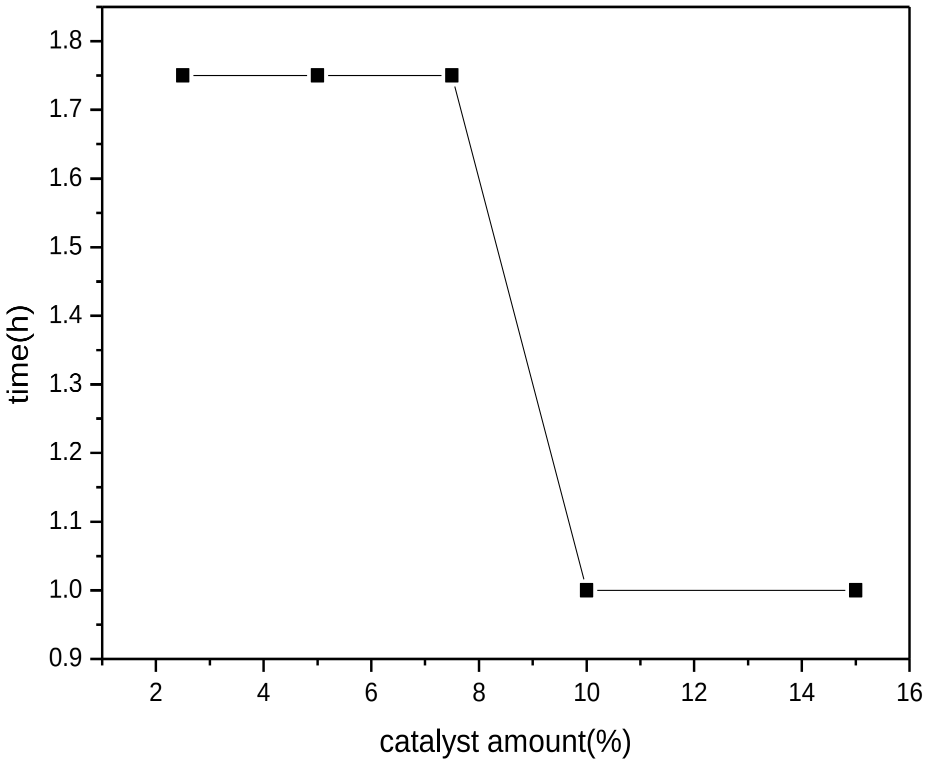


Figure 14. Effect of catalyst concentration on reaction time required for the complete transesterification of cottonseed oil.

3.2.4 Effect of calcination temperature

The catalyst prepared (5-Na_2CO_3/ZnO) was calcined at different temperatures to obtain the least transesterification time. Calcination temperatures were varied from 200–600 ºC. A series of reactions were conducted with cotton seed oil using 10 wt-% (catalyst/oil), 1:18 molar ratios of oil: methanol and reaction temperature of 65 ºC . Pattern as in Figure 15 was obtained.

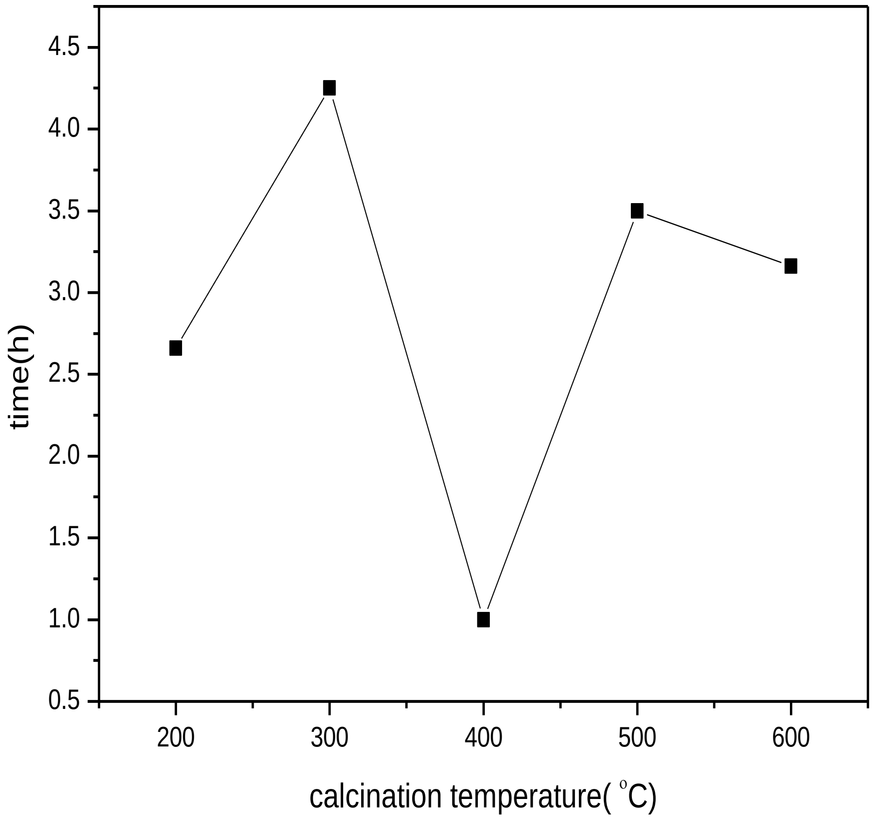


Figure 15. Effect of calcination temperature on reaction time required for the complete transesterification of cottonseed oil.

3.2.5 Effect of Reaction Temperature

A series of transesterification reactions was conducted in the presence of 10 wt-% (catalyst/oil) 5-Na_2CO_3/ZnO/400 to find the optimum temperature for the transesterification reaction. The time required for the complete transesterification of vegetable oil to biodiesel decreases from 10 h to 1 h as the temperature of the reaction was increased from 35 to 65 ºC. A further increase in the reaction temperature does not reduce the reaction time significantly as shown in Figure 16.

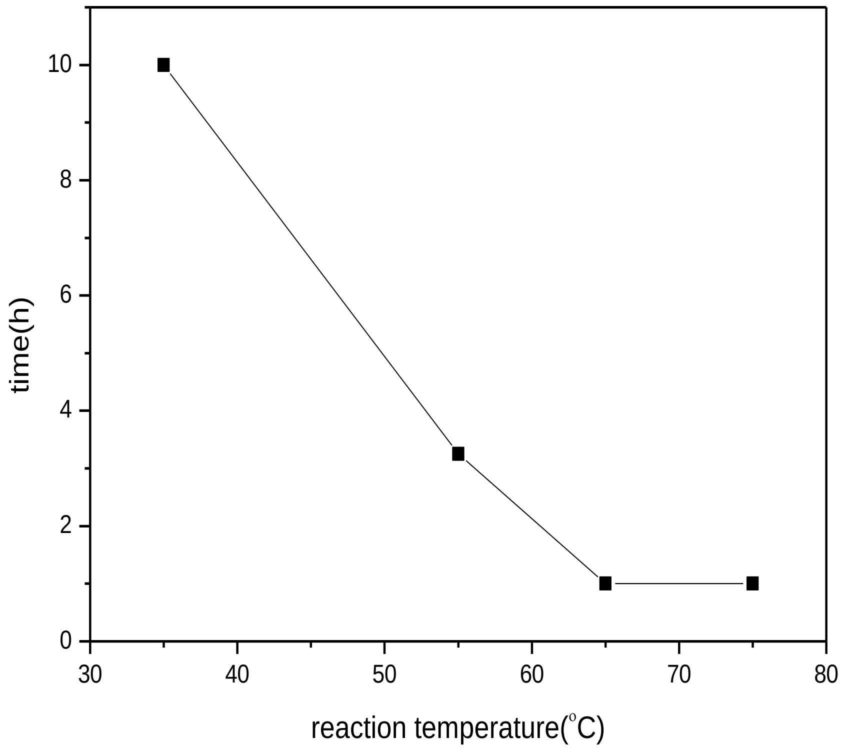


Figure 16. Effect of reaction temperature on reaction time required for the complete transesterification of cottonseed oil.

3.2.6 Effect of methanol/oil molar ratio

The stoichiometric requirement of transesterification reaction is 3 moles of methanol per mole of triglyceride to yield 3 moles of fatty esters and I mole of glycerol. However, with transesterification being a reversible reaction, usually such reactions performed with an excess of methanol shifts the equilibrium in the forward direction to achieve a maximum methyl ester yield. Heterogeneous catalysts usually catalyzed the transesterification reaction at a slower rate and took more time for the completion of the reaction. The use of higher molar ratios of oil to alcohol (viz., 1:15, 1:40, and even 1:275) to improve the yield of transesterified product in less time have been reported in the literature[52-54] when reactions were catalyzed by heterogeneous catalysts. A number of transesterification reactions were carried out using different oil/methanol molar ratios from 1:9 to 1:27 at 65 ºC and 10 wt-% of 5-Na_2CO_3/ZnO/400. The rate of transesterification reaction increases as the oil/methanol ratio was increased from 1:9 to 1:18, and the reaction was found to be completed in 1 h when a 1:18 ratio was taken. A further increase in the oil/methanol ratio does not increase the reaction rate significantly, and complete conversion still takes 1 h as shown in Figure 17.

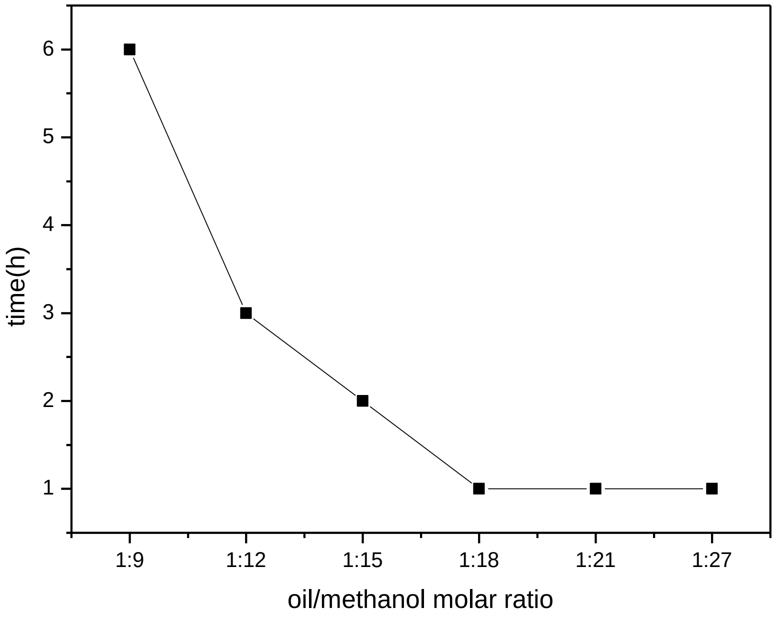


Figure 17. Effect of oil/methanol molar ratio on reaction time required for the complete transesterification of cottonseed oil.

3.2.7 Study with other feedstocks

Transesterification reactions of different oils and fat with varying fatty acid content were carried out with 10 wt-% (catalyst/oil) 5-Na_2CO_3/ZnO-400; 1:18 oil/methanol molar ratio at 65 ºC. Different methyl ester yield was obtained with different feedstocks as calculated by ^{1}H NMR and summarized in Table 5.

Table 5. Transesterification of different oils with 5-Na_2CO_3/ZnO-400 catalyst and 1:18 oil:methanol molar ratio at 65 ºC reaction temperature.

OIL	FFA content (wt-%)	REACTION TIME (h)	CONVERSION (%)*****
Cotton seed oil	0.1	1	97
Fat	0.85	4	99
Jatropha oil	8.4	32	22
Karanja oil	4.23	25	50

*****on the basis of ^{1}H NMR

CONCLUSION

The present work demonstrates the preparation of a series of metal ions (Na, Co, Ni, Cu) impregnated on ZnO and MgO supports and investigation of their catalytic activities towards transesterification of cottonseed oil. Zinc oxide impregnated with 5 wt-% sodium and calcined at 400 °C (5-Na_2CO_3/ZnO-400) was found to show the highest catalytic activity among the prepared catalysts. Based on the Powder X- ray diffraction studies, catalyst was found to exist in single hexagonal phase and in nano-particle form with average particle size of 46 nm. The catalyst, 5-Na_2CO_3/ZnO-400, when used for the transesterification of cotton seed oil, required only 1 h for the complete transesterification of the oil utilizing methanol to oil molar ratio 18:1 at 65 ºC. Same catalyst have been tested, under similar reaction conditions, for the transesterification of animal fat and found to complete the transesterification of the same with in 3 h of reaction duration. However, catalyst failed to catalyze the complete transesterification of the jatropha and karanja oil, could be due to the presence of high FFA contents in these oils. Presently studies are focussed in our lab to test the physico-chemical properties viz. (cloud point, pour point, kinematic viscosity, density, ash content, metal ion leaching) of the prepared biodiesel samples.

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