LITHIUM SUPPORTED MAGNESIUM OXIDE AS A HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION FROM MUTTON FAT

A

Thesis Submitted

in partial fulfilment of the requirement for the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

Submitted By:
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CERTIFICATE

*This is certify that the thesis entitled "**Lithium supported magnesium oxide as a heterogeneous catalyst for biodiesel production from mutton fat**" 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**, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and that no part of this project has been submitted for the award of any other degree.*

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

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CANDIDATE'S DECLARATION

I hereby declare that the work presented in this thesis entitled, ***"Lithium supported magnesium oxide as a heterogeneous catalyst for biodiesel production from mutton fat"*** *in partial fulfilment of the requirement for the award of Degree of* ***Master of Science in Chemistry****, submitted in* ***the School of Chemistry and Biochemistry, Thapar University****, Patiala, is an authentic record of my own work carried out under the supervision and guidance of* ***Dr. Amjad Ali****, Assistant Professor , School of chemistry and biochemistry, Thapar University, Patiala and refers other researcher's work which are duly listed in the reference section.*

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

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Place: Patiala

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Date: July, 2010
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Regards, Navjot Kaur
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ABSTRACT

In present thesis, Li ion impregnated MgO catalysts were prepared using wet impregnation method followed by calcinations, and prepared catalysts were used for the transesterification of animal fat 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 mutton fat were found to be depended on their basic strengths, amount of Li ion impregnated in MgO support, and calcination temperature. The catalyst with 5 wt-% Li ion doping in MgO support and calcined at 523 K were found to show the maximum catalytic activity and used to optimize the reaction condition for the transesterification reaction of mutton fat. The complete transesterification of the same with methanol (12:1 molar ratio, MeOH:fat) was observed in 37 minutes of reaction period at 65 °C.

1. INTRODUCTION

Over the past decades, there has been increase in the consumption of diesel and petroleum fuels. Due to diminution of these fossil resources and recent increases in petroleum price an uncertainties in its availability stimulated the search for substitutes for petroleum derivatives. The alternatives to diesel fuels are becoming increasingly important due to shortage of these non-renewable resources and the environmental consequences of exhaust gases from petroleum and diesel fuelled engines[1-3]. Among the purposed alternative fuels biodiesel has received much attention in recent years for diesel engines due to their advantages as it is made from renewable biological sources such as vegetable oils and animal fat. It is biodegradable, non-toxic, technically feasible, economically competitive, environmentally acceptable, has low emission profiles and readily available[4-6]. Biodiesel fuel, consists of fatty acid methyl esters (FAME), produced by the transesterification of vegetable oils and animal fats with methanol has the following characteristics: it is a biomass-derived fuel and is free from aromatic compounds, and it has high biodegradability and low SO_x and particulate matter content in diesel fumes. These characteristics improve combustion efficiency and emission profile[7]. Methyl esters of fatty acids are usually produced by transesterification of triglyceride to methyl esters using sodium or potassium hydroxide dissolved in methanol as homogeneous catalysts due to their low rates, effectiveness, low concentration, and heat requirements in the reaction[6,8,9]. The equation of the transesterification reaction is shown in Fig. 1.

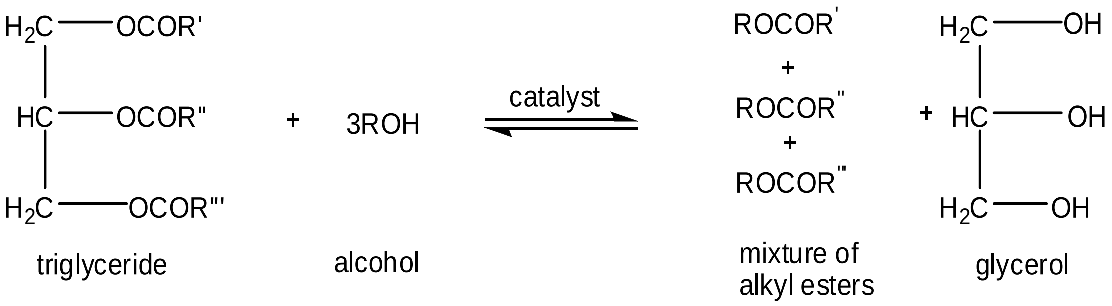


Fig. 1. Transesterification of vegetable oil or animal fat

2. LITERATURE REVIEW

Besides base catalysts, transesterification process also include Bronsted acids preferably sulfonic acid and sulphuric acid but with these catalysts the reactions are slow, requires high temperature and take more time for complete conversion [10,11]. The reaction in which these types of catalysts are used is called acid-catalyzed transesterification reaction. The acid catalyzed transesterification reaction requires anhydrous condition to avoid the formation of carboxylic acids which reduces the yield of alkyl esters. Since acid catalysts can simultaneously carry out esterification of (Free Fatty Acids) FFAs and transesterification of triglycerides, they could help in processing low-cost, low-quality feedstocks generally with high FFAs concentration, and thereby lowering overall production costs. Economical assessment of different biodiesel production processes using homogeneous alkali and acid catalysts, as well as heterogeneous acid catalysts and supercritical methods have been recently discussed in the literature[12].The results indicate that heterogeneous acid-catalyzed process is clearly advantageous over the other studied processes, as it has the highest rate-of-return, lowest capital investment, and technically is a relatively simple process. Likewise, in particular reaction conditions the acid catalyst can promote the *in-situ* transformation of glycerol into oxygenated-derivatives of interest for the formulation of biodiesel[l3]. However, some research studies dealing with transesterification reactions catalyzed by solid acids have been reported in the literature, while many papers are devoted to esterification reactions with solid acid catalysts—mainly acid resins[14]. Nevertheless, the commercial introduction of these catalysts still need important advances to impact in a positive way on the biodiesel synthesis technologies. Some improvements include aspects such as: increasing the stability of acid sites avoiding their leaching, increasing thermal stability, enhancement of mass transfer avoiding diffusional limitations, milder operation conditions by means of sufficient design of acid catalysts combining high activities and selectivity's for transesterification reactions, as well as resistance to water impurities usually present in unrefined feedstocks. Thus, it seems that an ideal acid solid catalyst should join the following characteristics[15]: interconnected system of large pores to minimize diffusional problems of molecules having long alkyl chains; moderate to high concentration of strong acid sites to promote the transesterification reaction with significant rates; high thermal stability of acid sites to minimize leaching effects and hydrophobic surface to promote the preferential adsorption of oily hydrophobic species on the catalyst surface and avoiding possible deactivation of catalytic sites by strong adsorption of polar compounds, especially water. The mechanism of acid catalyzed transesterification reaction is shown in Fig. 2.

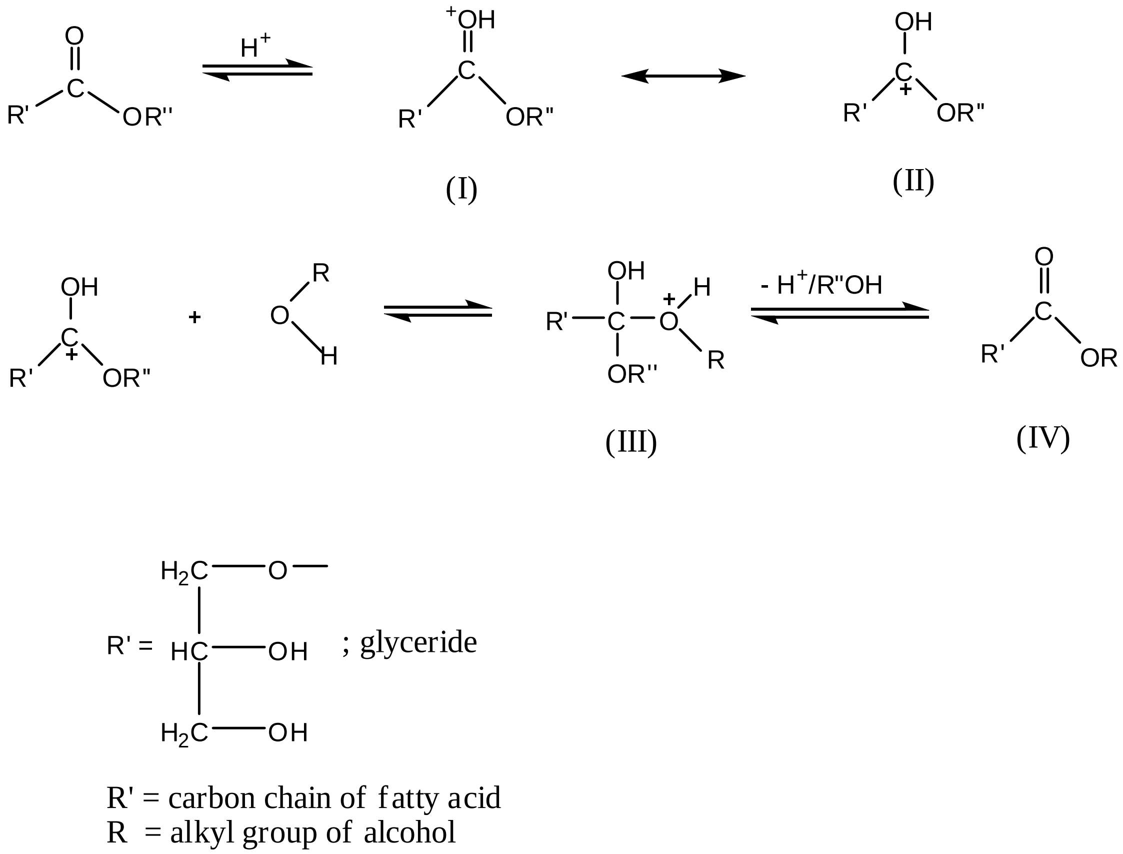


Fig.2. Mechanism of acid-catalyzed transesterification of vegetable oils or animal fats.

Among alkali catalysts alkali metal alkoxides and hydroxides as well as sodium or potassium carbonates are mostly used because they complete reaction in lesser time even at room temperature. The mechanism of base-catalyzed transesterification reaction of oils or fats is shown in Fig. 3. The technology based on the use of alkaline catalysts for promoting transesterification reaction requires less free fatty acid content and the absence of water. Because the presence of water gives rise to the formation of Free Fatty acids (FFA’s) by hydrolysis of some of the formed ester, with consequent soap formation. The reaction of FFA’s with the basic catalyst is shown in Fig. 4. Saponification reaction reduces the catalytic activity and causes serious disadvantages in product separation because of emulsion formation between the produced biodiesel and side product glycerol. It takes long settling time for the separation[10, 13].

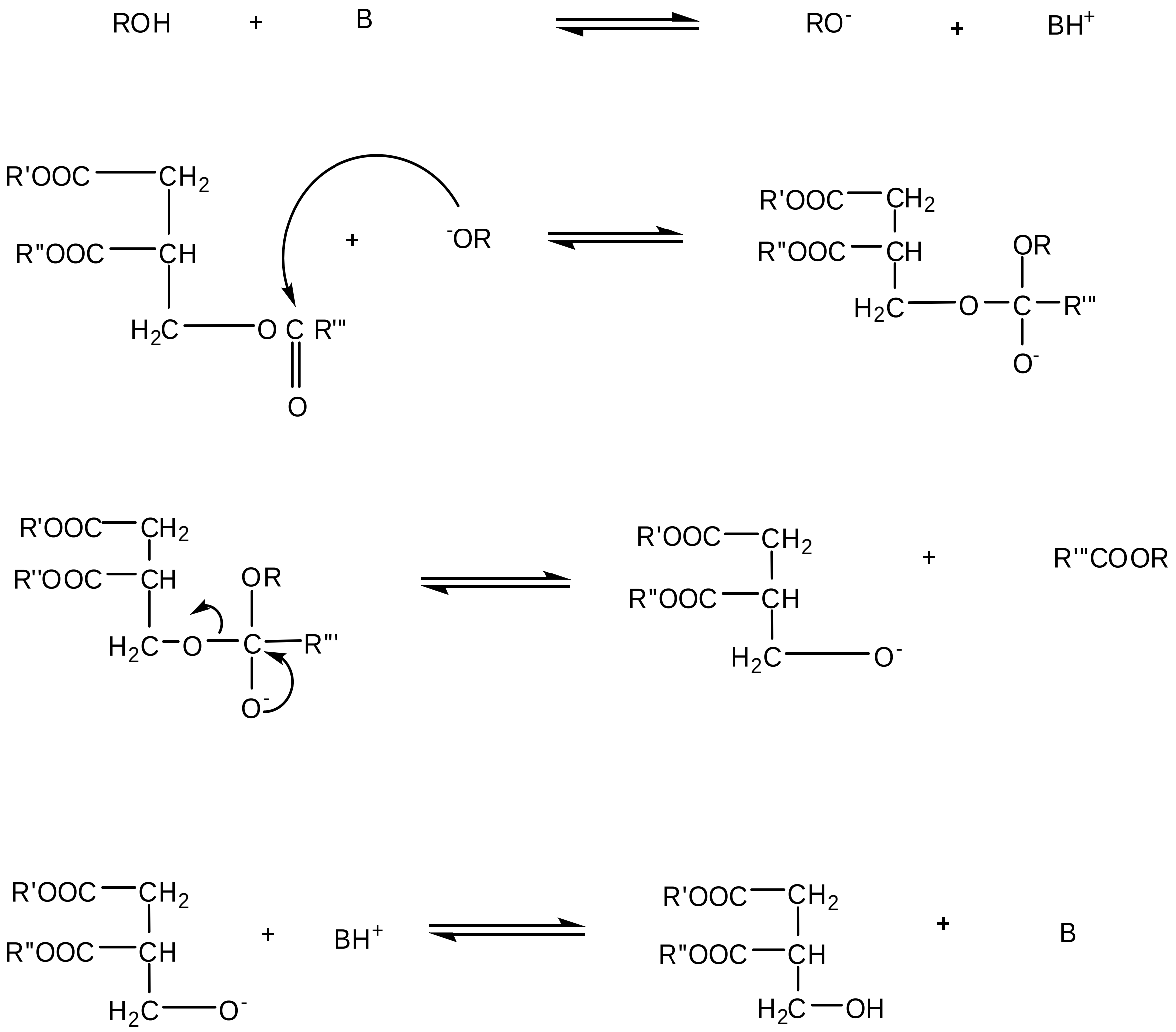
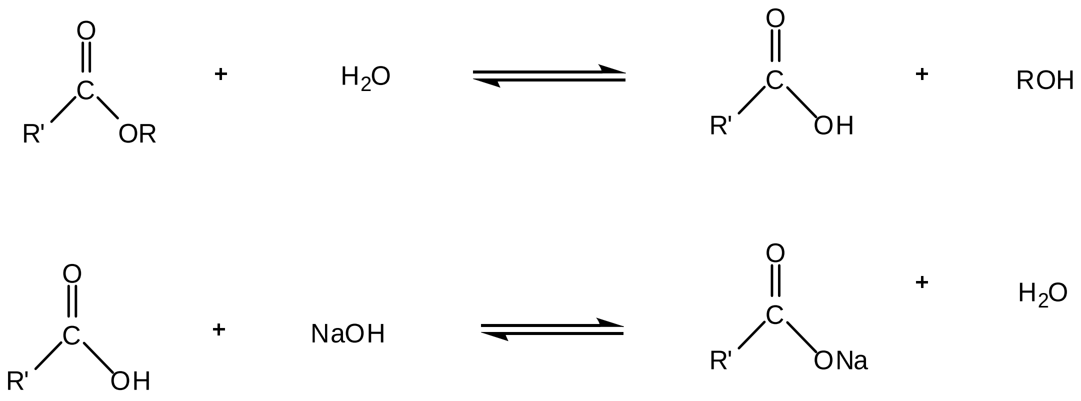


Fig. 3. Mechanism of the base-catalyzed transesterification of vegetable oils or animal fats

Several other methods have been proposed to solve these problems but the most useful seem to be the use of enzymes. Hydrolytic enzymes are readily available and easy to handle. They are stable in most water-immiscible solvents and do not require any coenzymes. The major problems associated with the application of lipase is, high production cost of lipase and inhibition of lipase activity by the glycerol, produced during the reaction[15]. The reaction yields as well as the reaction times are still unfavourable compared to the base-catalyzed reaction systems.



R' = carbon chain of the fatty acid
R = alkyl group of the alcohol

Fig. 4. Saponification reaction of FFA's with basic catalyst

Currently, nearly all biodiesel is produced via homogeneous catalysis, in which the catalyst must be separated from the biodiesel and glycerol what requires multiple process steps which are time consuming. Moreover the purification is a non-environmental-friendly process because involves the consumption of large amounts of water and the disposal of a highly basic streams which increases the overall cost of production.

Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. The use of heterogeneous catalysts for the synthesis of the renewable diesel-substitute biodiesel has many advantages over the homogeneous routes currently favoured by industry. Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are non corrosive, environmentally benign and present fewer disposal problems. They are also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer catalyst lifetimes.

In the heterogeneous process, the catalysts are very stable with no metal leaching; catalysts can be recycled and reused for long periods of time[16,17]. The development of basic heterogeneous catalysts for biodiesel production including carbonates and hydrocarbonates of alkaline metals; alkaline metal oxides; alkaline metal hydroxides; anionic resins, basic zeolites, *etc.*[18,19] can catalyze many types of chemical reactions, such as isomerization, Knoevenagel condensation, Michael condensation, transesterification[20-23] and oxidation .Various types of heterogenous catalyst[24] shown in Table 1.

Table 1: Types of few basic heterogeneous catalysts and their composition

Types of basic heterogeneous catalyst	Composition
Single component metal oxides	Alkali metal oxides Alkaline earth oxides Rare earth oxides ThO_2, ZrO_2, ZnO, TiO_2
Zeolites	Alkali ion-exchanged zeolite Alkali ion-supported zeolite
Supported alkali metal (or alkaline earth metal)	Alkali metal ions on alumina Alkali metal ions on silica Alkali metal on alkaline earth oxides Alkali metals and alkali metal hydroxides on alumina
Clay minerals	Hydrotalcites Crysotile Sepiolite
Non- oxides	Alkaline alkoxide Alkaline carbonate Guanidine-containing catalysts

Some researchers found MgO has low activity in transesterification of vegetable oils to biodiesel and CaO provides a slow reaction rate to reach an equilibrium state[25, 26]. Reddy et al.[27] produced biodiesel using nanocrystalline CaO under room temperature. But, the reaction rate was slow and it takes 6–24 h for complete conversion with their most active catalyst. They also observed deactivation after eight cycles with soybean oil and after three cycles with poultry fat. Zhu et al.[28] obtained a 93% conversion of jatropha curcas oil using CaO as a catalyst. But, the catalyst must be treated with an ammonium carbonate solution and calcinated at high temperature. Gryglewicz studied alkaline earth metal oxides, hydroxides and alkoxides to catalyze transesterification reaction [29,30].

Calcium methoxide, as a solid base catalyst has a moderate surface area, relative broader particle size distribution, narrower pore size distribution, strong basicity, long catalyst lifetime and better stability in organic solvent. Therefore, the stability and sustained activity of the catalyst are of great importance for industrial applications. Therefore, $Ca(OCH_3)_2$ can contribute much to decreasing the cost of biodiesel production due to its long catalyst lifetime and good stability as a heterogeneous solid base catalyst[31] . Different heterogeneous base catalysts such as $Na/NaOH/\gamma\text{-}Al_2O_3$[32], WO_3/ZrO_2[33] and Li/CaO[34,35] have been determined to be efficient for the transesterification reaction.

Recent studies have also found functionalized mesoporous silica, such as tin-oxide-modified mesoporous SBA-15[36] titanium-grafted mesoporous silica[37] and Mg-MCM-41[38] to be effective in catalyzing various transesterification reactions. However, there was no report of base-functionalized mesoporous silica being used to catalyze the transesterification of vegetable oil with ethanol for biodiesel production in the literature. The catalytic activities of various MgO functionalized mesoporous materials in the transesterification of vegetable oil were compared. Mesoporous catalysts were chosen because their acidic/basic properties can be easily modified by varying their surface groups and composition, and they have uniform structures and high surface areas, which are ideal as catalysts for large organic molecules and guest–host chemical supports[39]. In one study, supported CaO/MgO was used[40] for the transesterification of rapeseed oil at a relatively low temperature of 65 °C by impregnating on a MgO carrier, followed by the calcination at 700 °C in $Ca(Ac)_2$ solution. The catalyst showed higher activity with a glycerol yield of more than 80% purity. In other work[41] soybean oil was transesterified at 100 °C with methanol using MgO and calcined hydrotalcites (CHT) as catalysts. Four different basic sites were individuated at MgO and the calcined hydrotalcites for the transesterification, and the strongest basic site was able to perform the transesterification reaction at a temperature below 100 °C. More than 45% of biodiesel yield was observed in the case of MgO, and more than 75% yield was observed with CHT. At a higher temperature of 200 °C, more than 95% of FAME yield was observed for MgO and CHT. Biodiesel production with high surface area (HSA) nanocrystalline metal oxides on TiO_2, MgO, and CaO supports were investigated[42] M-Acetylacetonate (AcAc) was supported on the HSA support, where M was Na, K, Ca, Li, V, Fe, N, and Al. The best catalysts tested were CaO and AcAc supported on MgO and TiO_2.

In some earlier work of catalyst screening and their reaction kinetics determination[43] five different solid catalysts (MgO, CaO, BaO, PbO, and MnO_2) were used for the transesterification of soybean oil at 215 °C. Biodiesel yield of 85% in 14 min with

BaO and a yield of 84% in 85 min with PbO were achieved. In a different work, biodiesel production of jatropha curcas oil with a solid catalyst CaO dipped in ammonium nitrate followed by calcination at 900 °C showed an oil conversion of 93% at 70 °C for 3.5 h of transesterification. The catalyst dosages and the oil/methanol ratio used in the study were 1.5% and 9:1, respectively. In a different work of soybean oil transesterification[44] with SrO as a heterogeneous catalyst, a yield in excess of 95% was observed below 70 °C within 30 min. A long catalyst lifetime of SrO was also investigated because it sustained the activity after repeated used for 10 cycles.

Many studies about the use of heterogeneous catalysts for transesterification treated anti-leaching performance as issue of equal importance to catalytic activities. The deactivation mechanism of heterogeneous catalysts towards transesterification can be classified into the leaching of active species and the adsorption of acidic hydrocarbons onto basic sites[45]. Some of these catalysts have shown a good catalytic performance even under reaction conditions similar to those used for the homogeneous catalysts. The history of heterogeneous base catalysis is shorter than that of heterogeneous acid catalysis. Although well-known acidic materials also possess basic characters, base catalyses by solid materials were not utilized in the early developmental period, because the basic sites are easily covered with atmospheric components such as CO_2, H_2O, and O_2, which generate carbonate, hydroxide and peroxide, respectively, and incapacitate the function of the basic sites.

The most common drawback with the heterogeneously catalyzed process is its slow reaction rate compared with the homogeneous process. Due to this reason, the reaction conditions of heterogeneous catalysis are severe to enhance its slow reaction rates by increasing reaction temperature (100–250° C), catalyst amount (3–10 wt-%) and methanol/ oil molar ratio (10:1–25:1). Another drawback of the heterogeneous process is the dissolutions of active species into liquids, which makes the catalysis partly ‘homogeneous’ and then causes problems in biodiesel quality and limits the repeated use of catalyst.

Enhancement in the reactivity of nanosized oxides is associated with their increased surface area, greater concentrations of highly reactive edge and corner defect sites, and unusual, stabilized lattice planes[46]. Nanocrystalline calcium oxide is an efficient catalyst for the production of environmentally compatible biodiesel fuel in high yields at room temperature using poultry fat as raw materials. It was anticipated that the greater activity of nanosized oxides allow the transesterification of poultry fat to occur efficiently at room temperature, which would afford low energy consumption[47]. NaOH, an alkali hydroxide was used for transesterification of tallow fat for biodiesel production[48].

In the present work, a solid base catalyst of MgO loaded with lithium was prepared via an wet impregnation method and followed by calcinations. The catalytic efficiency of the catalysts in the transesterification of animal fat with methanol was investigated in detail, and more attention was given to the effects of calcination temperature and lithium loading amounts. In addition, the transesterification conditions (such as the amount of catalyst, the molar ratio of methanol to fat, and the reaction time) were optimized with the Li/MgO catalyst.

The presence of minor quantities of odd-numbered iso and anteiso branched-chain fatty acids in mutton fat has been proved by the isolation of 13-methyltetradecanoic acid, (+)-12-methyltetradecanoic acid, (+)-14-methylhexadecanoic acid and 10-methyldodecanoic acid. The isolation from hydrogenated mutton fat of trace quantities of an even-numbered iso acid, 16-methylheptadecanoic acid (isostearic acid), which has not formerly been present in any natural fat[49] and iso-butyric acid has also been reported. The trace component of n-decanoic acid is also present in mutton fat[50]. Various types of fatty acid composition (wt-%) in different oils[51] and animal fat[52] described in Table 2.

Table 2: Fatty Acid Composition (wt-%) of various Vegetable Oils and animal fat.

Fatty acid	**Soybean oil**	**Cotton seed oil**	**Palm oil**	**Coconut oil**	**Animal fat**
Lauric	0.1	0.1	0.1	46.5	-
Myristic	0.1	0.7	1.0	19.2	3
Palmitic	10.2	20.1	42.8	9.8	26
Stearic	3.7	2.6	4.5	3.0	14
Oleic	22.8	19.2	40.5	6.9	47
Linoleic	53.7	55.2	10.1	2.2	3
Linolenic	8.6	0.6	0.2	0.0	1
Palmitoleic acid	-	-	-	-	3

3 EXPERIMENTAL SECTION

3.1 Materials

Animal (mutton) fat collected from Patiala, Punjab, India, was used for the experimental studies. Magnesium oxide (MgO), AR grade was purchased from Merck, India. Lithium hydroxide monohydrate GR ($LiOH.H_2O$), lithium carbonate extra pure ($LiCO_3$), lithium nitrate ($LiNO_3$) hexane, ethyl acetate, acetic acid and methanol (Extra pure) and silica gel for thin layer chromatography were obtained from Loba Chemie, India and used as such without further purification.

3.2 Methods

Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical's X'Pert Pro with using monochromatic CuKα radiation (λ=1.54060 Å) in Thapar University, Patiala. Data were collected over a 2θ range of 5–80° with a step size of 0.0260° at a scanning speed of 2°/min. at an accelerating voltage of 45 kV and current of 40 mA. Field emission scanning electron microscopy (FESEM) was performed on JEOL JSM 6510LV to collect the SEM images of the catalysts. Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of biodiesel, animal fat and vegetable oils were recorded on a Bruker Avance-II (400 MHz) spectrophotometer. The basic strengths of the catalysts (H_) were determined by using Hammett indicators. Approximately 25 mg of the catalyst was added in 5 ml of a solution of Hammett indicators diluted with methanol and was left to equilibrate for 2 h. After the equilibration, the color of the catalyst was noted. The following Hammett indicators were used: 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).

3.3 Catalyst preparation

Lithium impregnated MgO catalyst for transesterification reactions were prepared by following the literature reported wet impregnation method[53] with slight modification. In a typical preparation (e.g., the preparation of 5-Li/MgO-523), 10 g of magnesium oxide was suspended in 150 mL of deionized water, and to this 10 mL aqueous solution containing 2.997 g of $LiOH.H_2O$ was added. The resulted slurry was stirred for 3 h, and then evaporated to dryness and heated at 120°C for 24 h and calcined at 523 K temperature for 8 h. Similarly catalyst were prepared using various amount of lithium ranging from 2-5 wt-% of MgO using, $LiOH.H_2O$, Li_2CO_3, and $LiNO_3$, as lithium ion precursors. Catalysts so prepared were characterized by Hammett indicator test, flame photometry, powder X-ray diffraction and SEM studies.

The catalysts prepared in such a manner were designated as XX-Li/MgO-T, where XX represents the wt-% of Li ion in MgO support and T calcination temperature in Kelvin, e.g., 5-Li/MgO-523 represents MgO catalyst formed by impregnation of 5 wt-% of Li^+ using $LiOH.H_2O$ salt and calcined at 523 K.

3.4 Transesterification of animal fat

In a typical transesterification, mutton fat (Mol wt, 890) and methanol in 1:12 molar ratio and 5 wt-% of catalyst of mutton fat 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. The set-up of transesterification reaction as shown in Figure 5.

Figure 5: Set-up of transesterification reaction.

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 animal fat with the selected solvent system, and complete conversion of animal fat to biodiesel was supported by the disappearance of the animal fat spot on the TLC plate. TLC analysis of animal fat, biodiesel standard and prepared animal fat biodiesel as shown in Figure 6.

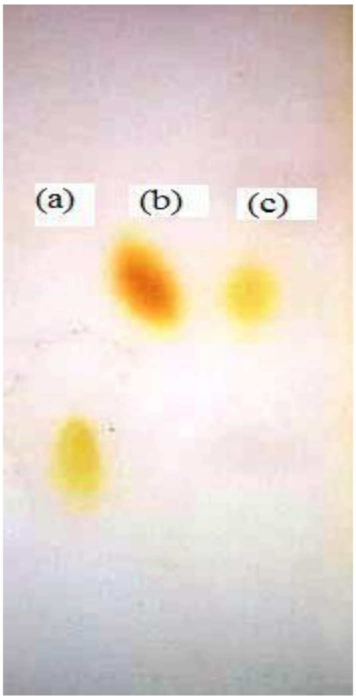


Figure 6: TLC analysis of (a) animal fat, (b) biodiesel standard and (c) prepared animal fat biodiesel.

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[54].

4. RESULTS AND DISCUSSION

4.1 Catalyst characterization

The basic strengths of the catalysts were determined by using the Hammett indicators and summarized in Table 1. The basic strength of 5-Li/MgO-523 catalyst was found to be maximum, $18.4 < H\_ <$, among the prepared catalysts, probably due to the formation of strong basic sites on the MgO surface. Hence, the catalyst 5-Li/MgO-523 is expected to show the highest catalytic activity toward the transesterification reaction of animal fat.

Powder X-ray diffraction studies of MgO and different lithium ion concentration impregnated (2-5%) MgO have been performed, and comparisons of XRD patterns are given in Figure 7. The intense peaks at 2θ ~ 36.80, 42.85, 62.28, 78.59 correspond to the d-values of 2.44, 2.11, 1.49, 1.21 respectively, of magnesium oxide, while peaks at 2θ ~18.51, 37.97, 50.71, 58.62 correspond to d-values of 4.79, 2.36, 1.80, 1.57 respectively, of magnesium hydroxide as shown in Figure 7. Indexing of MgO and $Mg(OH)_2$ was done on the basis of JCPDS card no. 87-0653 and 86-0441. The particle size of the catalyst was determined by the Debye-Scherrer method[55] using powder XRD data and found to be about 17 nm. Based on the Powder X- ray diffraction studies, catalyst was found to exist in single hexagonal phase in nano-particle form.

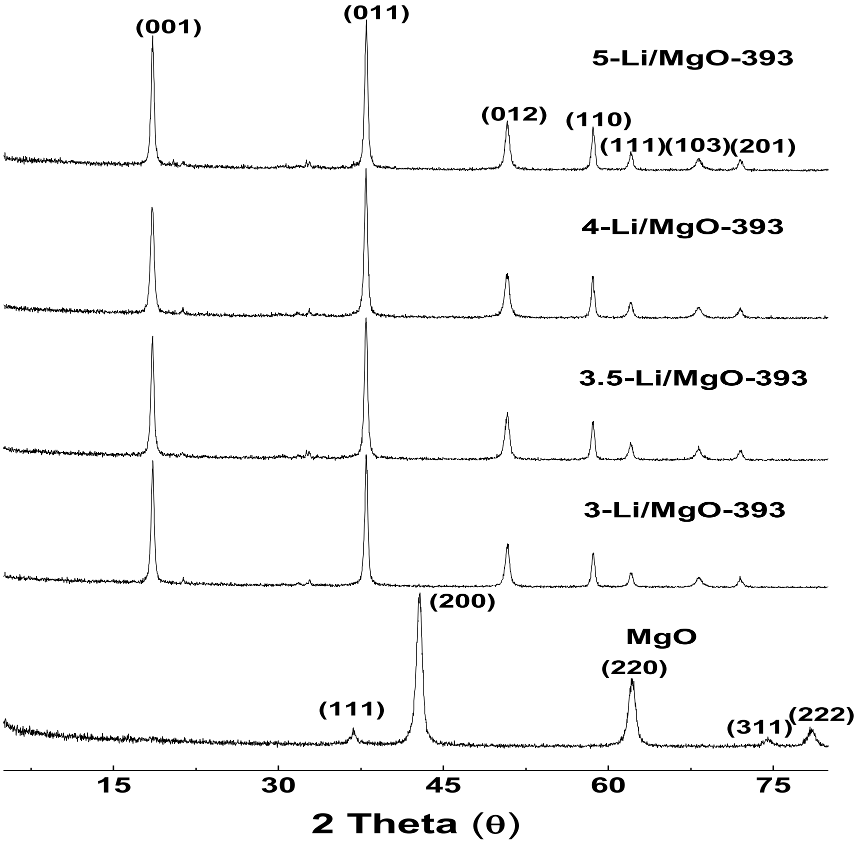


Fig. 7. Comparison of powder XRD patterns of commercially available MgO with 3-5 wt- % Li impregnated MgO.

With increase in calcination temperature of catalyst the particle size was found to be increased and basic strength found to be decreased. The particle size was found to be minimum, ~ 17 nm, for 5-Li/MgO-523 and basic strength was found to be maximum, 18.4<H_< for the same and hence it expected to show the highest catalytic activity towards transesterification reaction. Comparison of XRD patterns of pure MgO with 5 wt-% Li loaded MgO and calcined at temperatures ranging from 523 K to 923 K as shown in Fig. 8. Comparison of basic strength and particle size of different catalysts summarized in Table 3.

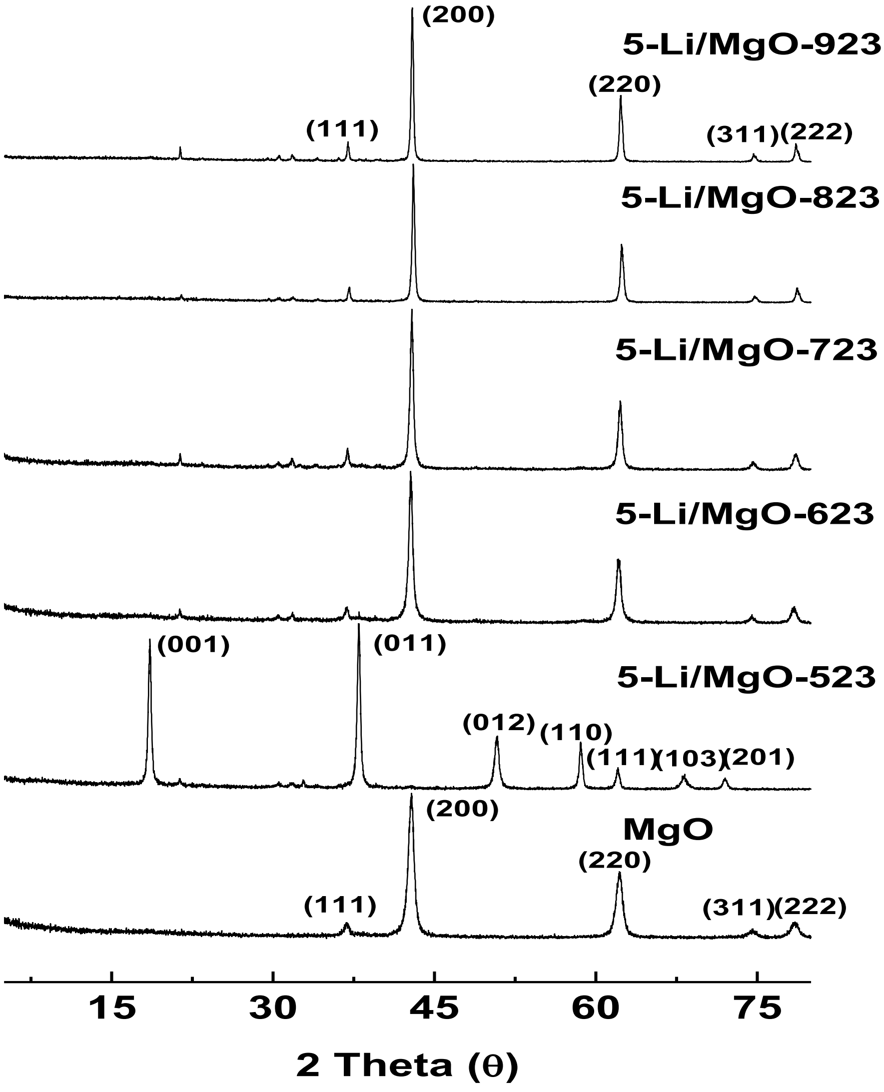


Fig. 8. Comparison of XRD patterns of pure MgO with 5 wt-% Li loaded MgO and calcined at temperatures ranging from 523 K to 923 K.

Table 3. Comparison of basic strength and particle size of different catalysts.

S.No.	Catalyst	Particle size (nm)	Basic strength
1	3-Li/MgO-393	16.8	15.0<H_<18.4
2	3.5-Li/MgO-393	18.2	-
3	4-Li/MgO-393	18.3	-
4	5-Li/MgO-393	16.9	-
5	5-Li/MgO-523	16.8	18.4<H_<
6	5-Li/MgO-623	17.3	15.0<H_<18.4
7	5-Li/MgO-723	19.6	15.0<H_<18.4
8	5-Li/MgO-823	22.7	15.0<H_<18.4
9	5-Li/MgO-923	25.5	-

The surface morphology of the catalyst 5-Li/MgO-523, have been investigated by scanning electron microscopy shown in Fig. 9. The average size of the porous and oval shaped catalyst particles by FESEM studies was found to be ~ 50 µm. Particle size measurement by powder XRD studies revelled that these particles are the clusters of further smaller particles with average size of 17 nm.

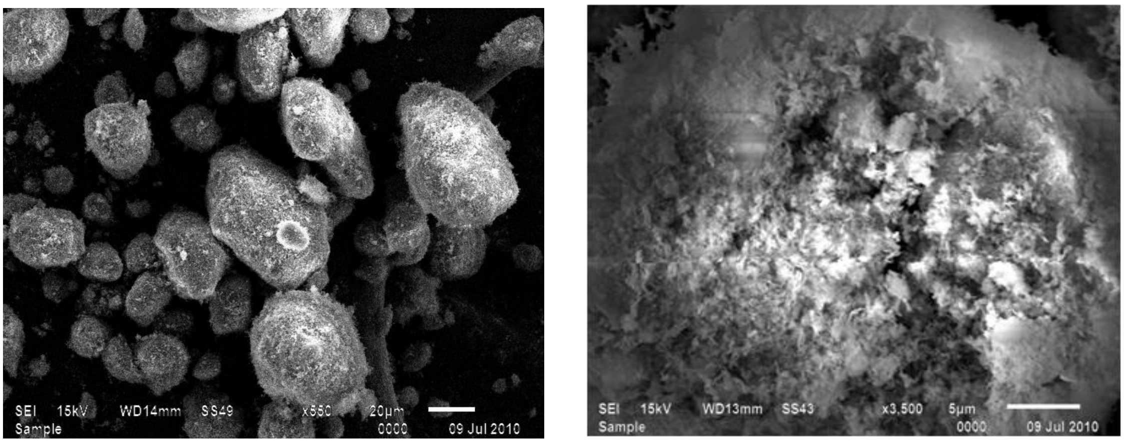


Fig. 9. SEM images of 5-Li/MgO-523.

4.2 Transesterification Reactions and Biodiesel Characterization

Transesterification reactions of mutton fat with methanol (1:12 molar ratio) were performed in the presence of prepared catalysts (5 wt-%, catalyst/fat) at 65 °C. Prepared catalysts were used to carry out the transesterification reactions of mutton fat in order to determine the minimum time for the completion of the transesterification reaction. During the course of work, the following parameters have been varied (i) different lithium salts (ii) impregnated lithium ion concentration, (iii) calcination temperature (iv) reaction temperature, (v) fat/methanol molar ratio (vi) study with different feedstocks (Soybean oil, Cotton seed oil, Karanja oil, Jatropha oil).

Biodiesel produced in the transesterification reaction was characterized by ^{1}HNMR spectroscopy. The proton NMR spectrum of fat shows a multiplet at 4.1 ppm due to the presence of glyceridic protons along with other hydrocarbon-proton peaks at their normal positions[56]. The appearance of a new peak at 3.6 ppm due to -OCH_3 protons and disappearance of the glyceridic protons support the formation of biodiesel as shown in Fig.10.

Similarly formation of biodiesel was confirmed from soybean and cotton seed oil due to the presence of a new the peak at 3.6 ppm due to -OCH_3 protons and disappearance of the glyceridic protons. The proton NMR spectra has also been used to confirm the completion of the reaction (99.5 % conversion of animal fat to biodiesel) by following the methods as reported in the literature[57,58].

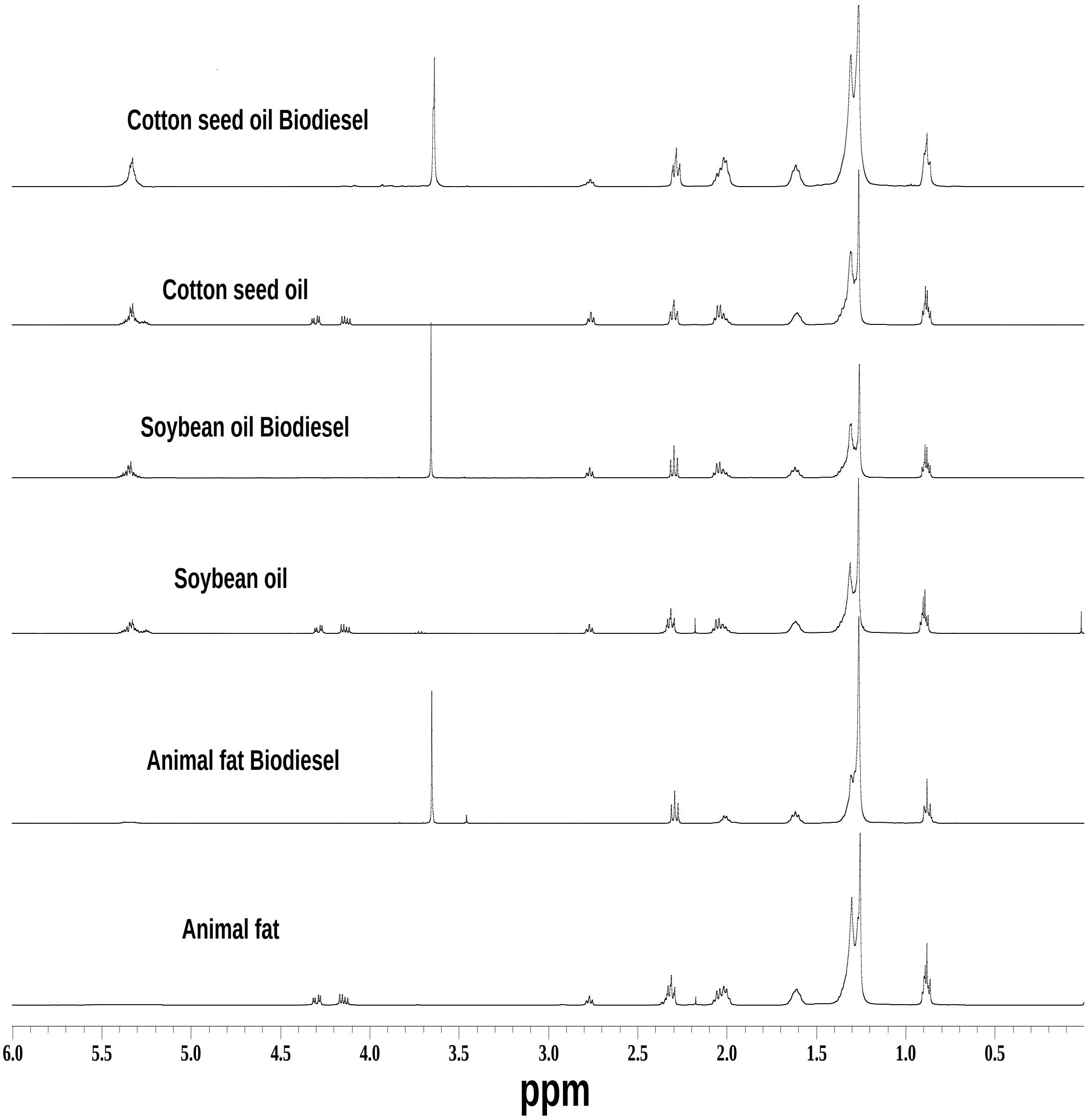


Fig. 10. Comparison of the ^{1}H NMR spectra of oil/fat with that of corresponding biodiesel.

4.2.1 *Effect of different lithium salts on catalytic activity*

Salts of lithium metals such as carbonate and nitrates have also been used for catalyst preparation besides hydroxide. The same procedure for the preparation (wet impregnation) can be used for these salts. Use of different salts may vary the chemical properties such as basic strength of the catalysts. The transesterification reaction was not complete with carbonate and nitrate salts of lithium.

4.2.2 *Effect of impregnated lithium ion concentration*

To determine the optimum amount of lithium ion impregnation in MgO, a series of catalysts by varying the amount of lithium ion from 2-6 wt-% (Li^+ ion/MgO) in MgO were prepared. Transesterification of mutton fat was performed with methanol (1:12 molar ratio) at 65 °C in the presence of 5 wt-% of prepared catalysts. The reaction time required for the complete transesterification was found to decrease from 3 h to 37 min as the amount of lithium ion in MgO was increased from 2-5 wt-%. However, a further increase in Li^+ ion concentration does not reduce the reaction time as shown in Fig. 11 hence, 5-Li/-MgO catalyst was used for transesterification reactions to optimize other parameters for achieving the minimum time for the completion of the transesterification reaction.

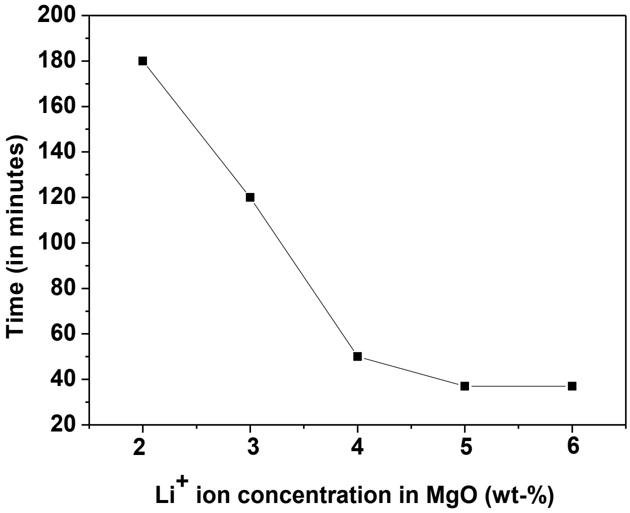


Fig. 11. Effect of lithium ion concentration on the reaction time required for complete transesterification of animal fat.

4.2.3 *Effect of calcination temperature*

The transesterification reaction time increases with increase in calcination temperature of the catalyst. The catalyst calcined at 523 K took minimum time for the completion of the reaction. So the transesterification reactions were further studied with a catalyst 5-Li/MgO-523 for optimization of other parameters. Effect of calcination temperature on the reaction time required for complete transesterification of animal fat as shown in Fig. 12.

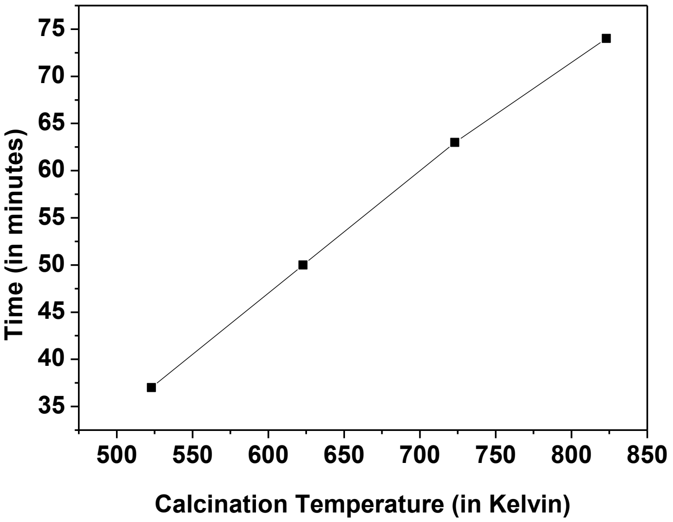


Fig. 12. Effect of calcination temperature on the reaction time required for complete transesterification of animal fat.

4.2.4 *Effect of reaction temperature*

A series of transesterification reactions was conducted in the presence of 5 wt-% (catalyst/fat) of 5-Li/MgO to find the optimum temperature for the transesterification reaction. The time required for the complete transesterification of animal fat to biodiesel decreases from 1 h 20 min to 15 min as the temperature of the reaction was increased from 45-75 °C. A further increase in the reaction temperature does not reduce the reaction time significantly as shown in Fig. 13.

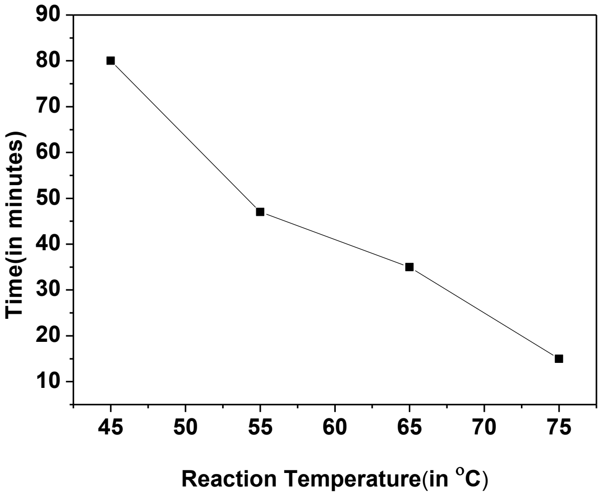


Figure 13: Effect of reaction temperature on the reaction time required for complete transesterification of animal fat.

4.2.5 *Effect of Fat/Methanol Molar Ratio*

The effect of the fat/methanol molar ratio on the transesterification reaction is one of the important parameters which affects the methyl ester yield as well as cost of the biodiesel production. The theoretical minimum fat to methanol molar ratio should be 1:3 for the complete conversion of animal fat to biodiesel. 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/fat 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[59-61] when reactions were catalyzed by heterogeneous catalysts. To determine the optimum fat/methanol molar ratio, the reactions were performed with 1:3 to 1:21 molar ratios using 5-Li/MgO-523 catalyst at 65 °C. The transesterification reactions were not completed with 1:3 and 1:6 (Fat:MeOH). The rate of transesterification reaction increases as the fat/methanol ratio was increased from 1:9 to 1:12, and the reaction was found to be completed in 37 min when a 1:12 ratio was taken. A further increase in the fat/methanol ratio does not increase the reaction rate significantly, and complete conversion still takes 37 min as shown in Figure 14.

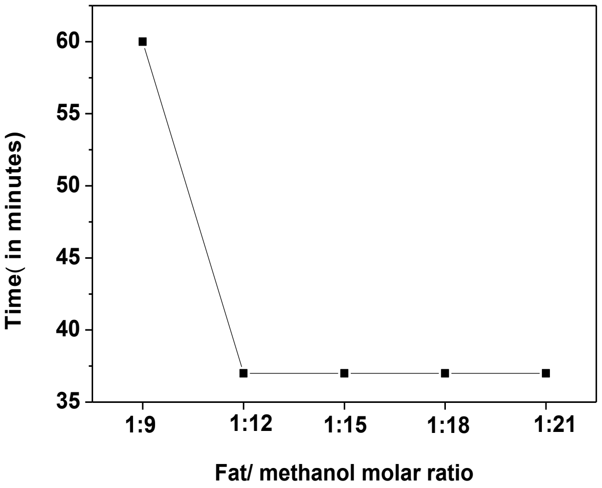


Fig. 14. Effect of the fat/methanol molar ratio on the reaction time required for complete transesterification of animal fat.

4.2.6 Catalytic activity with vegetable oil

The catalyst, 5-Li/MgO-523, has also been used for the transesterification of a variety of vegetable oils viz., Soybean oil, Cotton seed oil, Karanja oil and Jatropha oil as shown in Table 4. The transesterification reaction was found to be completed within 20 minutes in case of soybean and cotton seed oil. On the other hand when, jatropha and karanja oil, were used as feedstock reaction didn't yielded the complete conversion even after 11 h of reaction period. This observation could be explained due to the presence of high amount of FFAs present in such feedstocks.

Table 4. Efficiency of the catalyst, 5-Li/MgO-523, for the transesterification of vegetable oils. All reactions were performed at 65 °C using 12:1 molar ratio of methanol/oil.

S. No.	**Oil**	**FFAs (wt-%)**	**Reaction time (h)**	**Conversion**
1	Soybean	0.22	0.3	> 98 %
2	Cotton seed	0.33	0.3	> 98 %
3	Karanja	4.3	11	Incomplete
4	Jatropha	8.4	11	Incomplete

5. CONCLUSIONS

The present work demonstrates the preparation and characterization of lithium ion impregnated MgO catalysts and investigation of its catalytic activity toward the transesterification of animal fat. Magnesium oxide impregnated with 5 wt-% lithium and calcined at 523 K (5-Li/MgO-523) was found to show the highest basic strength as supported by Hammett indicator tests. Based on the Powder X- ray diffraction studies, catalyst was found was found to exist in single hexagonal phase and in nano-particle form average particle size of 17 nm. The catalyst, 5-Li/MgO-523, when used for the transesterification of mutton fat, required only 37 min for the complete transesterification of the fat utilizing methanol to fat molar ratio 12:1 at 65 ºC. Same catalyst have been tested, under similar reaction conditions, for the transesterification of vegetable oils and found to complete the transesterification of Cotton seed oil and Soybean oil with in 20 min of reaction duration. However, catalyst was failed to catalyze the complete transesterification of the jatropha and karanja oil, could be due to the presence of high FFAs present 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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