TRANSESTERIFICATION OF TRIGLYCERIDE USING POTASSIUM IMPREGNATED Mg/Al HYDROTALCITE

A

Thesis submitted

In the partial fulfillment of the requirement for the degree of

MASTERS OF SCIENCE

IN

CHEMISTRY

Submitted By

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UNDER THE SUPERVISION OF

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THAPAR UNIVERSITY,

PATIALA-147004

2017

CERTIFICATE

This is to certify that the thesis entitled **"Transesterification of Triglyceride Using Potassium Impregnated Mg/Al Hydrotalcite"** submitted by **Mr. Nishant Thakur** in the partial fulfillment of the requirements for the degree of **Master of Science in Chemistry** from **Thapar University, Patiala,** is a bonafied piece of work carried out under the guidance and supervision of **Dr. Amjad Ali,** Associate Professor and Head, School of Chemistry and Biochemistry, Thapar University, Patiala and no part of this project has been submitted for award of any other degree in this or any other university.

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

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SELF DECLARATION

The work embodied in the project entitled **"Transesterification of Triglyceride Using Potassium Impregnated Mg/Al Hydrotalcite"** has been done by me in the partial fulfillment of requirement for the award of degree of **Masters 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 and Head, School of Chemistry and Biochemistry, Thapar University, Patiala. All the ideas and references have been duly acknowledged.

Date: 08/Aug/2017

Place: Patiala

Nishant Thakur

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

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Place: Patiala

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TABLE OF CONTENT

ABSTRACT

A series of K loaded LDH mixed oxides were prepared by wet impregnation method and their catalytic activities were explored for transesterification of triglyceride. The physico-chemical properties of the catalysts were evaluated by powder XRD, SEM-EDS and Mapping, TGA, and FT-IR studies. The prepared catalyst was successfully employed for the transesterification of waste cottonseed oil (WCO). The catalytic amount of 5wt% of 10-K^+/LDH catalyst (with respect to oil), shown higher conversion (~97%) of biodiesel compared to other catalysts amount. ^{1}H-NMR and ^{13}C-NMR techniques were employed to quantify the FAME yield obtained during the transesterification reaction.

CHAPTER 1

INTRODUCTION AND LITRATURE REVIEW

1.1 INTRODUCTION

Due to the steady growth in population as well as lot of industrial development, the demands for fossil fuels are quickly increasing day by day. Fossil fuel means are restricted, nonrenewable in nature and bound to deplete, hence there is need to replace it with the renewable sources. Biofuels are gaining a lot of interest and admiration in the field of research. Atmospheric carbon dioxide released by cars is a major greenhouse gas responsible for global warming which rapidly increases the importance of biofuels. Biofuels are actually a comprehensive term used for any kind of fuel derived from living matter so that gasoline and diesel comes under the category of biofuels. The only variance is that new age biofuels are made from plants where as the ancient biofuels are made from fossils or from decomposed plants and animals buried millions of years ago. Various kinds of biofuels are used in countries around the world today with major stress given on ethanol fuels. Various other types of biofuels are bio-alcohol, biodiesel, green diesel, bio-ethers, biogas, algae-based fuels, bio-hydrogen etc.

Biodiesel is an ecological, unconventional diesel fuel prepared from native renewable resources i.e. vegetable oils (edible or non-edible oil) and animal fats, that runs in diesel engines-cars, buses, trucks, construction equipment, boats, generators, and oil home heating units (Bajpai *et.al*., **2006**). Many countries all over the world are using eatable fatty oils such as rapeseed, palm, soyabean, sunflower, linseed, coconut oil etc. as a raw material for biodiesel production. In addition to edible oils, non-edible oils such as tallow or used frying grease and oil have not been reported well for the production of biodiesel. Other non-edible tree-based oil has great potential of being transesterified for making biodiesel. Biodiesel can be produced from straight vegetable oil, fats and waste cooking oil being reacted with short chain alcohols usually methanol and sometimes ethanol. The process used to convert these above feedstocks to biodiesel is known as **Transesterification.** In transesterification, ester group from waste cooking oils or fats (triglycerides) was separated to form tri alkyl ester molecule as shown in **Fig 1**. These reactions were often catalyzed by the addition of an acid or base. The method of transesterification was affected by the mode of reaction conditions i.e.; alcohol to oil molar ratio, type of alcohol, type

and amount of catalysts, reaction time, temperature and purity of reactants. We can monitor transesterification reactions by various techniques like TLC, GC, HPLC, ^{1}H NMR and IR.

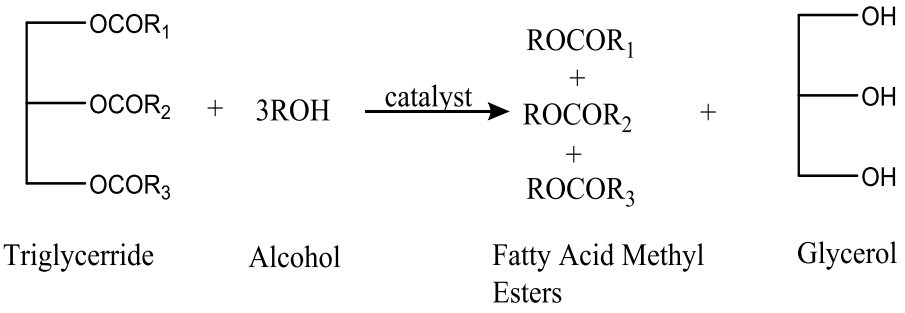


Fig 1. Transesterification of the triglycerides and R_1, R_2 and R_3 are straight hydrocarbon chain of fatty acids.

The alcohol used in transesterification reaction is methanol due to the economical reason (Demirbaş **2003**). New generation biodiesel proposes to originate from algae and other feedstocks which provide sustainability to the energy sources desired to effectively complement to the biodiesel trade. Irrespective of feedstock used for biodiesel synthesis, a catalyst is required to complete the reaction in significant time. There was a case where catalyst was not required for biodiesel production when alcohol and oil were used in supercritical conditions (Juntarachat *et.al*., **2014**). Catalyst can be synthesized by various methods including co-precipitation (Taufiq-Yap *et.al*., **2014**), wet impregnation (Kumar and Ali., **2013**) and sol-gel. Catalysts are mainly categorized into two broad categories such as homogeneous and heterogeneous. Earlier, the biodiesel production 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 biocatalyst possessing high selectivity and also belong to the group of homogeneous biocatalysts. However, high cost of biocatalyst restricted their application for the biodiesel production at industrial scale. To decrease the cost of biodiesel production, some researchers have developed new biocatalysts in recent years. An advantage is that no purification is required while using these biocatalysts (Fukuda *et.al*, **2001** and Talha *et.al*., **2016**). The limitations of homogeneous catalysts can be avoided by the use of heterogeneous catalysts that can reduce the additional running costs associated with the stages of separation and purification. In addition, heterogeneous catalyst doesn't leads to formation of soap through FFA (free fatty acid) neutralization and triglyceride (vegetable oils or animal fats) saponification. For a catalyst

to be heterogeneous in nature, it would not leach into the reaction mixture and must be reused. Yield of biodiesel depends on different parameters such as types of oils, alcohol to oil molar ratio, temperature and catalysts amount.

1.2 LITRATURE REVIEW

Transesterification reaction of vegetable oils or animal fats was carried out *via* catalytic or non-catalytic approach. In case of non-catalytic approach, reaction took place under supercritical conditions which were an energy exhaustive process (Juntarachat *et.al*., **2014**) and require high temperature and pressure. A catalytic process involved biocatalyst (lipase) and chemical catalyst. The selection of the catalysts depended on the quantity of free fatty acids (FFA) existing in the oils. For oils had low FFA content, basic catalysts (NaOH, KOH, $KOCH_3$, etc.) were preferred while for those oils had high FFA content, acid catalyzed (HCl, H_2SO_4, etc.) esterification trailed by transesterification in presence of alkaline catalyst which was suitable.

1.3 CATALYSTS

In literature several category of catalysts have been applied for biodiesel production. Broadly catalysts can be classified into homogeneous catalysts, heterogeneous catalysts and biocatalysts as briefly described below.

1.3.1 Homogeneous Alkali Catalysts

Industrially biodiesel was produced by mainly utilizing homogenous alkali catalysts like NaOH, KOH, etc. (Dorado *et.al*., **2004**) for transesterification reactions. The chief advantage of utilization of homogeneous alkali catalysts was their high activity even at ambient conditions, low cost and readily available. The yield was reported 89-95%. The two-step reaction process was superior than single-step because lower temperature was required for this reaction with minimum amount of methanol and high amount of catalyst was achieved. However, these catalysts in feedstock were extremely sensitive towards water content (>0.1wt%) and FFA content (>0.6wt%). Due to high water content, the soap formation took place **(Fig 2)** with decrease in the ester yield and made the separation of glycerol from methyl ester difficult due to increase in viscidness and emulsion formation (Scott *et.al*., **1997**). Both homogeneous acidic and basic catalysts counteracted at the end of the reaction and detached from the products through washing with water that generated vast amount of industrial wastes.

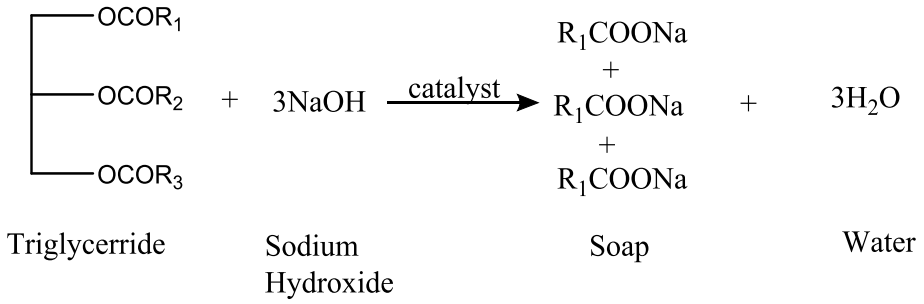


Fig 2. Saponification of fatty acids in presence of alkali, where R_1, R_2 and R_3 = straight hydrocarbon chains of fatty acid.

1.3.2 Homogeneous Acid Catalysts

The short comings of homogenous alkali catalysts might be avoided by means of homogeneous acid catalysts like H_2SO_4 (sulphuric acid), HCl (hydrochloric acid). They were generally active for the transesterification of vegetable oils or animal fats having more than 1% FFA (free fatty acids) contents. Normally they required harsh reaction conditions as compared to homogeneous base catalysts such as high temperature, high molar ratio of methanol to oil and long reaction interval. Acid catalysts were generally used for the two-step transesterification of feed stocks with free fatty acid (FFA) content greater than 1wt%. Firstly, acid catalyst was used for esterification of FFA with alcohol (mainly methanol) followed by acid neutralization and then transesterification by base catalyst.

1.3.3 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 washing of the product was not required. Heterogeneous catalysts were broadly 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: pyrolysis synthesis, physical mixing, wet impregnation and co-precipitation. To attain high catalytic activity for transesterification reaction combination of these methods has been used. But, the utmost combination used for catalyst preparation with high catalytic activity for transesterification reaction was impregnation followed by calcination (Kaur and Ali., **2014**).

1.3.3.1 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. Used carbohydrate derivative of solid acid catalysts were insoluble in the tried solvents and liquid reactants (water, methanol, n-hexane, t-butanol, oleic acid and WCO (Lou *et al*., **2008**).

1.3.3.2 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 KF/ZnO (Xie *et.al*., **2006**), CaO (Bankovi Ili *et.al*., **2017**), Nano-magnetic KF/CaO-Fe_3O_4 (Hu *et.al*., **2011**).

The mixed oxide synthesized catalysts comprising of CaO and ZrO_2 with various Ca to Zr molar ratios were used for transesterification of waste cooking oil (WCO) as feedstock with methanol to produce biodiesel at 65°C and 1 atm pressure. The experimental results specified the raise in activity of synthesized catalysts as the molar ratio from Ca to Zr increases but at the same time the firmness of the catalysts decreases (Molaei *et.al*., **2012**).

Hydrotalcites (HTs) are heterogeneous basic catalysts. Layered double hydroxides (LDHs) are also known as anionic clays. Hydrotalcites have anionic exchange capacity and also have the capability to capture the organic and inorganic anions which made them almost unique as inorganic materials. The potential applications of HTs were in ion-exchange/adsorption, pharmaceutics, photochemistry and electrochemistry. The hydrotalcites can also decomposed to mixed oxides with H_2O and loss of CO_2 (LDH carbonate form) by heating. The mixed oxides formed were getting particular interest due to their high basicity relative to the LDH precursor, increased surface area and homogeneous mixing of the different elements. LDHs have various applications in the field of medicine to synthesize drugs, additives in polymers, formation of composite nanomaterials, precursors to metal oxides catalyst and for removal of various environmental hazards (Frederic., **2012**).

These HTs have very strong alkali sites and are highly stable with decent adjustability of conformation and structure. However, the influential factors for the base-catalyzed activities

such as catalytic activity, Mg/Al molar ratio and calcination temperature were affected by low surface area. HTs with a 3:1 molar ratio of Mg to Al have the highest basicity and activity (Xie *et.al*., **2006**). Decomposition of HTs after calcination leads to high surface area of Mg-Al mixed oxide, which apparently exposed strong Lewis basic sites. According to reported literature (Xie *et al*., **2006**), transesterification process was carried out for 9 h with refluxing of methanol, methanol/soybean oil molar ratio of 15/1, catalyst amount of 7.5wt% and oil conversion rate was only found to be 67%. In the work of Brito *et al*., (**2009**) waste oil was used as a feedstock, biodiesel production was performed at temperatures ranging from 80 to 160ºC, methanol/oil molar ratio from 12/1 to 48/1 and catalyst concentration from 3-12wt%, respectively and 90% biodiesel yield was achieved. To get better activity of HTs catalysts the specific surface area of catalyst should be improved. (Guo and Fang., **2011**).

Hydrotalcites have two attractive features which impart catalytic properties to the materials. Firstly, the brucite-like layers have an abundance of basic sites allowing the materials to be used as heterogeneous solid base catalysts. Secondly, the two or more metal cations within the brucite-like layers are uniformly distributed at the atomic level without a segregation of ‘‘lakes’’of separate cations and where one of the cation was catalytically active transition metal that lead to high catalytic activity and selectivity. In LDHs varying the amount of divalent cations such as Mg^{2+} was substituted with trivalent cations such as Al^{3+}. LDHs were also prepared by certain cations such as zinc, calcium, copper, nickel, gallium and iron. Hydrotalcites was also known as anionic clays with formula $[M^{2+}_{(1-x)}\ M^{3+}_{x}(OH)_2] \cdot yH_2O$ where $M^{2+}$and M^{3+} are the divalent and trivalent metal cations (Chang *et.al*., **2013** and Brito *et.al*., **2009**). LDHs exhibited favorable characteristics for the adsorption of pollutants such as large surface areas, good thermal stabilities, and high sorption and regeneration efficiencies. Numerous modern studies have reported that calcined LDH has shown moderate activity in transesterification reactions.

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	**Reaction Temp (ºC)**	**Methanol/Oil -Molar Ratio**	**Catalyst amount (wt %)**	**Reaction Time**	**Yield (%)**	**References**
Ca MgO/Al_2O_3	60	60:1	10	3	85.3	Taufiq-Yap *et.al*.,**2014**
K-CaO	65	12:1	7.5	2	98	Kumar *et.al*.,**2012**
$CaAl_2$-LDH	65	6:1	1	5	90	Sankara *et. al*.,**2012**
Mg/Al/CO_3LDH	65	24:1	6	6	95	Brito *et.al*.,**2009**
CaO	60	13:l	1	1.5	90	Granados *et.al*.,**2007**

CHAPTER 2

RESEARCH GAP AND OBJECTIVES

2.1 RESEARCH GAP

In previous studies according to reported literature (Xie *et al*., **2006**), transesterification process was carried out for 9 h with refluxing of methanol, methanol/soybean oil molar ratio of 15/1, catalyst amount of 7.5wt% and oil conversion rate was only found to be 67%. In the work of Brito *et al*., (**2009**) waste oil was used as a feedstock, biodiesel production was performed at temperatures ranging from 80 to 160ºC, methanol/oil molar ratio from 12/1 to 48/1 and catalyst concentration from 3-12wt%, respectively and 90% biodiesel yield was achieved. To get better activity of HTs catalysts the specific surface area of catalyst should be improved. (Guo and Fang., **2011**).

In the present study the K-doped LDH is prepared by wet impregnation method. Transesterification reaction was carried out with the prepared catalyst by varying one parameter at a time (a) Effect of impregnated K^+ concentrations on LDH (b) amount of catalyst with respect to oil (c) methanol to oil molar ratio and (d) reaction temperature. The reusability of catalyst also studied.

2.2 OBJECTIVES

1. To prepare layered double hydroxides (hydrotalcites) as heterogeneous catalyst for transesterification of triglyceride by co-precipitation method.

2. To impregnate the prepared layered double hydroxides (LDH) with K by wet impregnation method.

3. To characterize the catalyst by Powder XRD, SEM-EDS and Mapping, TGA and FT-IR techniques.

4. To evaluate the stability and reusability of the catalyst.

5. To study the kinetics of transesterification reaction.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 MATERIALS and METHODS

Aluminium chloride ($AlCl_3$), Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$), hexane, ethyl acetate, and methanol were obtained from Spectrochem Pvt. Ltd. (India) and used as such without further purification. Waste Cottonseed Oil (WCO) used for the transesterification reactions was procured from local restaurants of Patiala, Punjab and found to have 4.4% of free fatty acid contents. Silica gel G for TLC was obtained from Loba Chemie.

Powder X-ray diffraction **(XRD)** framework were recorded on a **PANalytical's X'Pert pro** diffractometer operating at 40kV by skimming the samples over 2θ angle range of 5-90º with scanning rate of 2º per minute.

Scanning electron microscopy **(SEM)** recorded on **JEOL JSM 6510LV**. For analysis, initially sample was sonicated in ethanol for 2 h. A drop of this suspension was taken on a sample holder with the help of carbon tape. The sample was then coated with gold and visualized with instrument to assess the particle morphology.

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}.

Thermo gravimetric analysis **(TGA)** spectra were recorded on a **50 Shimadzy Corp 00568**. TGA of an uncalcined catalyst is done in the range between 0°C to 800°C under an inert nitrogen atmosphere. Before the sample is subjected to TGA the sample is first dried at 60°C in oven for 30 min. In TGA analysis, the sample is placed on a sensitive balance and heated in a controlled manner under nitrogen gas flow and is run with the rate of 10° per minute. The weight of the sample was continuously examined as the temperature is changed. The profile of weight change plotted against temperature can provide valuable information regarding the thermal behavior of the sample.

Fourier transform-nuclear magnetic resonance **(FT-NMR)** spectra of waste cooking oil and FAME'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). The FAME yield was calculated by 1H-NMR (proton nuclear magnetic spectroscopy) using reported formula (Knothe, **2001**).

$$\% \text{ FAME yeild} = \frac{2I \text{ (methoxy)}}{3I \text{ (methylene)}} \times 100$$

Where I (methoxy) and I (methylene) are the areas of methoxy protons (3.6 ppm) and methylene protons (2.33 ppm) respectively in the ^{1}H NMR of FAMEs. An inaccuracy of ±2% was detected when the FAME yield was computed by above method.

3.2 CATALYST PREPARATION

a. Hydrotalcites of Al and Mg were prepared by co-precipitation method following the literature reported procedure (Hincapi *et.al.*, **2017**). For the synthesis of LDH, mixture of $AlCl_3$ (10 mmol) and $MgCl_2.6H_2O$ (30 mmol) solution stirred at room temperature for 30 min. To this added 0.15 M sodium hydroxide (NaOH) aqueous solution and then slurry was stirred for 2 h at room temperature. The slurry was centrifuged and washed four to five times with deionized water to remove Cl^-. The product, thus obtained, was dried at 100ºC for 12 h and finally calcined at 500ºC for 4 h.

b. The prepared LDH was employed as support for the K impregnation. 10g of LDH was suspended in 40ml of deionized water. To this, 10ml of aqueous solution of potassium hydroxide (0.1M) was slowly added with vigorous stirring for 3 h and resulting precipitate was dehydrated at 120^{o}C for 12 h in oven which was finally calcined at 400 to 800^{o}C for 4 h in a muffle furnace.

The catalysts thus prepared was categorized as x-K^+/LDH-T, where x and T were potassium concentrations (wt%) and calcination temperature (ºC), respectively.

3.3 TRANSESTERIFICATION OF WASTE COOKING OIL (WCO) WITH LDH

The transesterification reactions were carried out in double neck round bottom (rbf) flask furnished with water cooled reflux condenser, magnetic stirrer and oil bath. In a reaction, 10g of waste cooking oil with desired amount of methanol and catalyst were stirred (500 rpm) at 65ºC temperature. The development of reaction was observed by withdrawing the sample from the reaction mixture after every 15 min with the help of capillary. The liquid thus obtained was

diluted with hexane and was subjected to TLC which was developed using silica gel as stationary phase and hexane/ethyl acetate (95/5, v/v) as mobile phase.

3.4 TRANSESTERIFICATION OF WASTE COOKING OIL (WCO) WITH K^+/LDH

Transesterification is a reversible reaction, and hence an extra amount of alcohol was added to force the reaction in the forward direction. The alcohol to oil molar ratio of stoichiometry reaction is 3:1, to produce 3 moles of biodiesel and 1 mole of glycerol. The transesterification reactions were carried out in 50 ml double neck round bottom (rbf) flask furnished with water cooled reflux condenser, magnetic stirrer and oil bath. In a transesterification reaction, 10g of waste cooking oil with desired amount of methanol and catalyst were stirred (600 rpm) at 65ºC temperature. The development of reaction was observed by withdrawing the sample from the reaction mixture after every 10 min with the help of capillary. The liquid thus obtained diluted with hexane and was subjected to TLC which was developed using hexane/ethyl acetate (95:5, v/v) as mobile phase and silica gel used as stationary phase. Production of biodiesel was identified by comparing its Rf (Retention Factor) value with standard sample of methyl oleate.

Fig 3. Image of TLC analysis of (a) methyl oleate standard (0.7), (b) waste cooking oil (0.5) and (c) waste cooking oil derived FAME (0.7).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CATALYST CHARACTERIZATION

4.1.1 SEM-EDS Study and Mapping

The shape, size of Layered Double Hydrotalcites (LDH) particles were observed by SEM as shown in **Fig 4**. The **Fig 4a** showed that LDH exists as irregular agglomerated particles having irregular geometry and size. On K incorporation, a significant change in catalyst morphology was observed it was found to attain the apple shape as shown in **Fig 4b**.

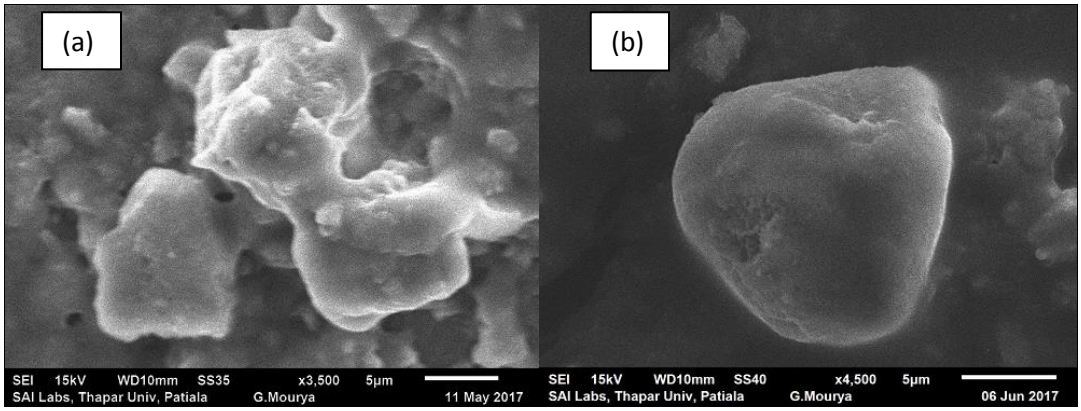


Fig 4. SEM image of (a) Layered Double Hydroxides (LDH) (b) K-doped LDH (10-K^+/LDH-550).

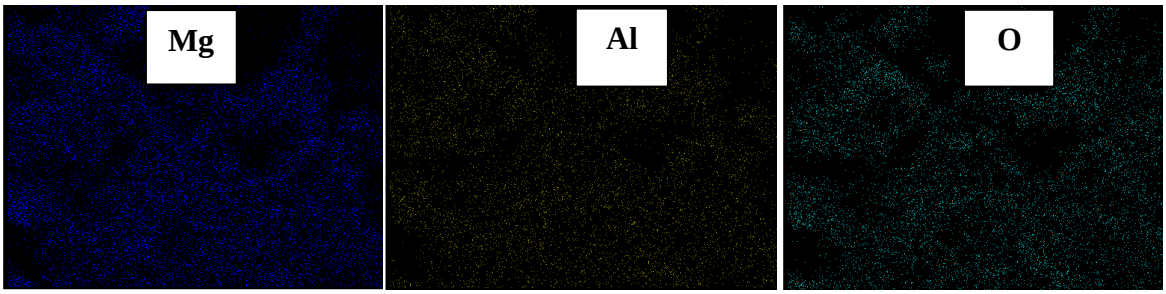
Qualitative analysis of the elements present in LDH and 10-K^+/LDH-550 was performed by EDS study. The analysis supported the presence of 32.04wt% magnesium and 12.97wt% aluminiumn early showing the ratio 3:1 of Mg: Al, in LDH. In case of K^+/LDH, along with Al and Mg, 5.76wt% of K was also observed as shown in Table 1.

Table 1. Showing composition of various elements.

Catalyst/Element	O (wt%)	Al (wt%)	Mg (wt%)	K (wt%)
LDH	43.50	12.97	32.04	-
K^+/LDH	48.97	12.11	33.16	5.76

Color mapping is shown in **Fig 5**. **Fig 5a** shows mapping images of LDH and **Fig 5b** shows mapping images of prepared catalyst K^+/LDH. The elemental mapping supports the homogeneous distribution of all elements over the catalyst surface.

(a)



(b)

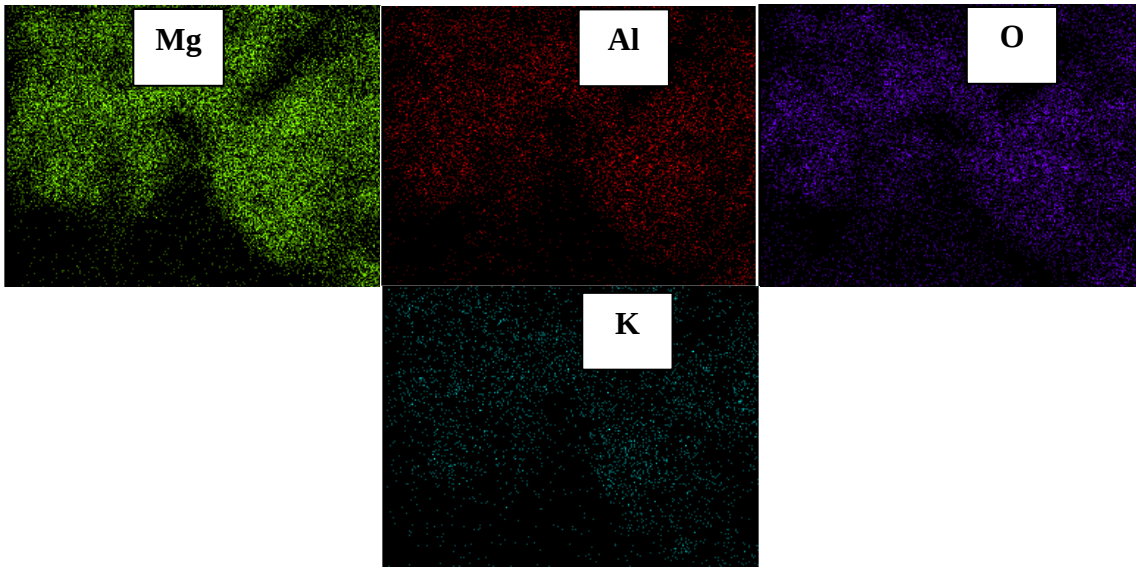


Fig 5. (a) Color mapping showing Al, Mg, O elements in LDH and (b) showing Al, Mg, O and K elements in K^+/LDH.

4.1.2 Thermo gravimetric Analysis (TGA)

Thermo gravimetric curve of as prepared K^+/LDH catalyst was demonstrated in **Fig 6**, which showed three weight loss regions. The first weight loss (12wt%) region was at 100°C - 250°C corresponds to the water elimination. The second weight loss (22wt%) region at 400°C - 500°C showed the dehydroxilation of brucite like layers and the third weight loss (7wt%) was in the

region between 700°C-800°C showed the decomposition of chloride ions in the interlayer region (Rozov *et.al.*, **2010**)

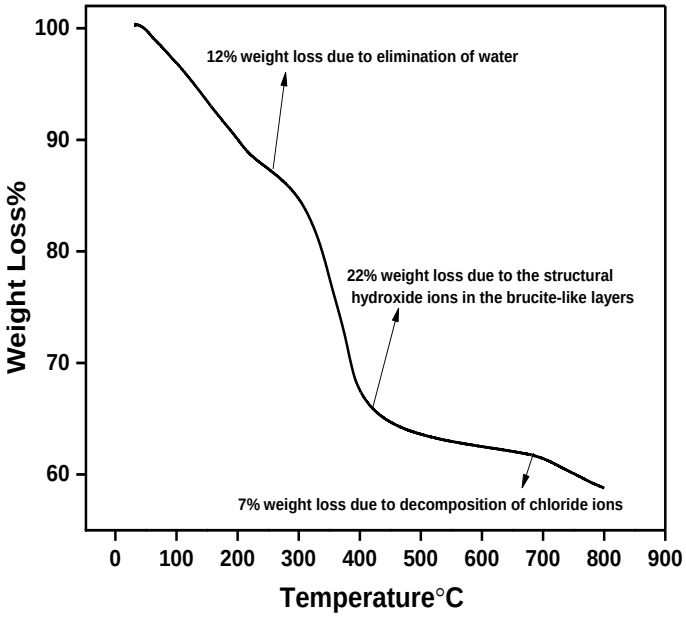


Fig 6. TGA curve showing weight loss of K^+/LDH catalyst at different temperature.

4.1.3 Power X-Ray Diffraction Study

The typical XRD patterns of the LDH were shown in **Fig 7**, showing the characteristic diffraction peaks at 2θ of 11.3°, 22.7°, 34.4°, and 61.3°. XRD diffractogram showed that as prepared LDH sample was found to have AlOCl and AlO(OH) in orthorhombic phase as supported by the observed data with that of JCPDS card no. 01-074-1864 and 01-072-1268, respectively. The other crystalline phases were of $Mg(OH)_2$ and Al_2MgO_4 having hexagonal and cubic shape, respectively as supported by the matching of diffraction data with JCPDS card no. 01-082-2455, 01-089-1627, respectively. Al_2MgO_4 with JCPDS card no. 00-001-1157, MgO with JCPDS 00-001-1235, AlO with JCPDS card no. 01-075-0278 were found to be present in calcined LDH (calcination temperature 500^{o}C), and all were present in cubic form. After 10wt% K loaded on LDH some new peaks appeared. The $K_2Al_{24}O_{37}$ (hexagonal) diffraction peaks were supported with JCPDS card no 00-001-1301, MgO (cubic), $MgAl_2O_4$ (orthorhombic) and $Mg_{0.4}Al_{2.4}O_4$ (cubic) were found with JCPDS card no. 01-087-0653, 01-084-0378 and 00-033-0853, respectively. The crystalline size (25nm) of prepared catalyst was calculated with the help of Scherrer equation (Sun *et.al.*, **2017**).

$$\mathrm{Dp} = \frac{0.94\lambda}{\beta_{\frac{1}{2}} \cos\theta}$$

Where Dp = Average crystalline size, $\boldsymbol{\beta}$= Line broadening in radians, θ= Bragg angle and λ= X-ray wavelength.

Table 2. Tabulated description of various compounds along with their JCPDS card no.

S.No	Symbol	Compound	Structure	JCPDS No.
1	*	MgO	Cubic	01-087-0653
2	□	$K_2Al_{24}O_{37}$	Hexagonal	00-001-1301
3	♣	AlO	Cubic	01-075-0278
4	φ	Al_2O_3	Orthorhombic	00-052-0803
5	◊	AlOCl	Orthorhombic	01-074-1864
6	○	$Mg(OH)_2$	Hexagonal	01-082-2455
7	●	Al_2MgO_4	Cubic	01-084-0378
8	♦	$Al_{2.4}Mg_{0.3}O_4$	Cubic	00-048-0528
9	♥	AlO(OH)	Orthorhombic	01-072-1268

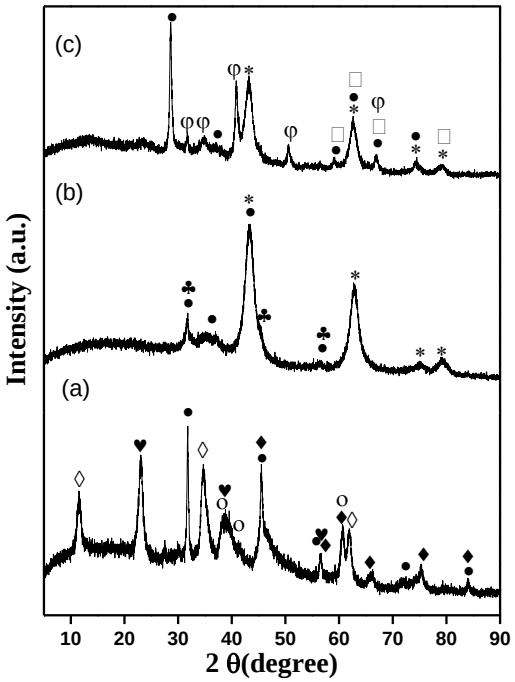


Fig 7. XRD pattern of (a) Uncalcined LDH (b) Calcined LDH (c) K^+/LDH.

4.1.4 FTIR study

In the FTIR spectra **(Fig 8)** of uncalcined LDH the band observed at 3742 $cm^{-1}$was due to the -OH stretching of water molecules and at 3408 cm^{-1} due to -OH stretching of hydroxides of Mg and Al. A strong peak around 1357 cm^{-1} was appeared in the spectra of uncalcined LDH, which corresponds to the characteristic peak Cl^- of interlayer anions. The appearance of a sharp band at 1357 cm^{-1} without any distinct degeneration indicated the absence of splitting of ν_3 band. Sharp peak at 1357 cm^{-1}, broad peak at 3408 cm^{-1} are characteristic peaks of an LDH structure. In K doped catalyst a sharp peak at 1523 cm^{-1} is appeared.The peaks and bands in the 400–1000 cm^{-1} region were associated with M-O and (M = Mg and Al) stretching modes in the LDH layers (Costa *et.al*., **2008**).

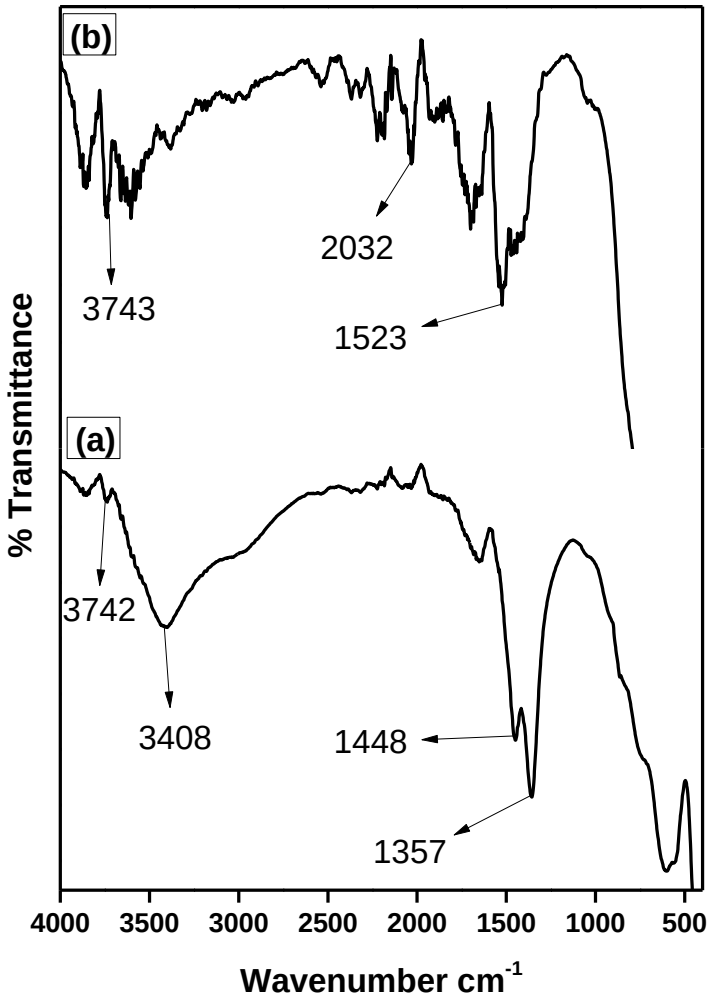


Fig 8. FTIR spectra showing (a) LDH (b) prepared K^+/LDH.

4.2 BIODIESEL CHARACTERIZATION

Proton NMR technique is not only non-destructive but also did not require complex 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 glyceride proton signals at 4.15-4.35 ppm, as shown in **Fig 9**. On transesterification, same peaks were not found in proton NMR spectrum of FAME. Moreover, the formation of FAME was further supported due to appearance of new peaks at 3.6 ppm (singlet).

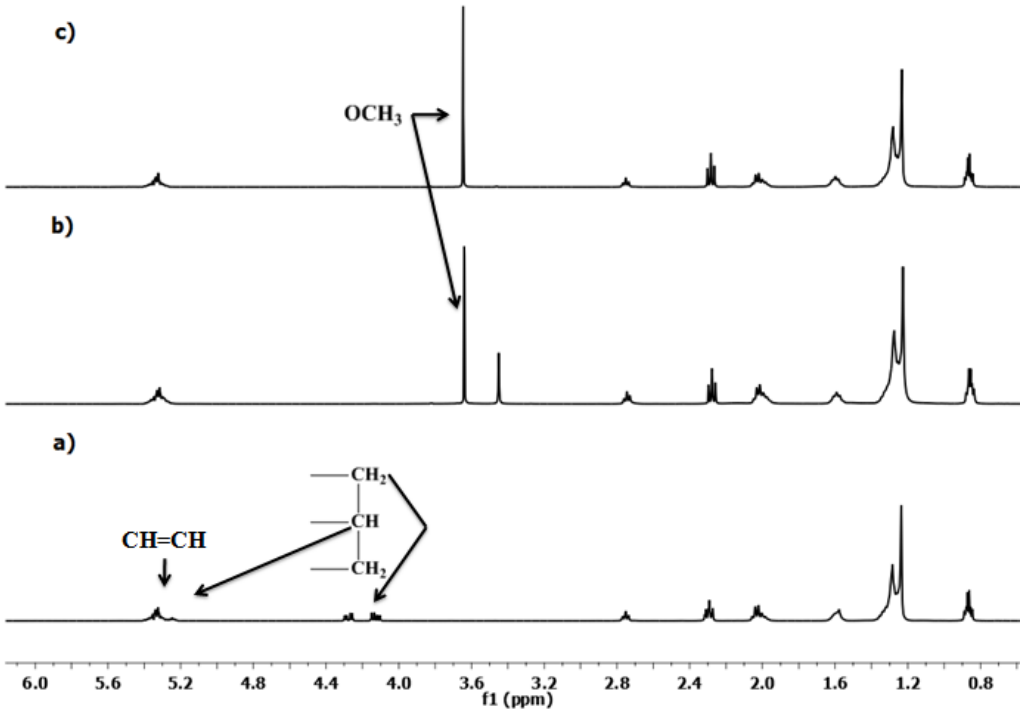


Fig 9. Comparison of ^{1}H-NMR spectra of (a) waste cooking oil (b) 5-LDH derived FAME (c) 10-K^{+}/LDH derived FAME.

In ^{13}C-NMR spectrum of WCO, signals due to glyceride carbon appear at 62.2 and 69.0 ppm, as shown in **Fig 10**. The formation of FAME could also be supported due to appearance of peaks at 51.4ppm due to $-OCH_3$ carbons. Further, peaks corresponding to the glyceride carbons were no longer found in ^{13}C-NMR spectrum of FAME.

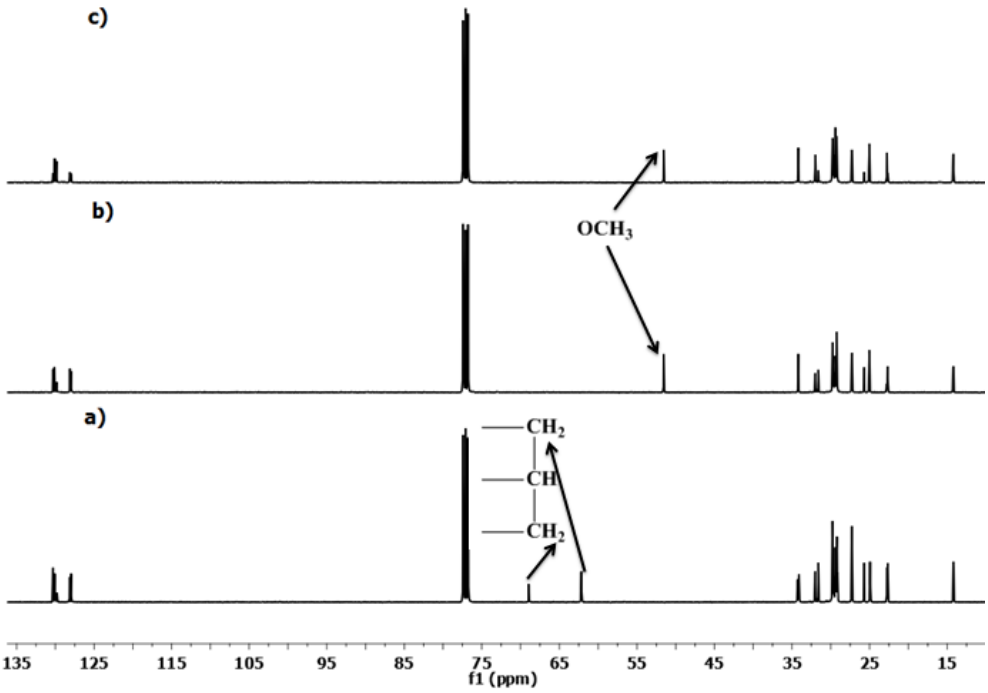


Fig 10. Comparison of ^{13}C-NMR spectra of (a) waste cooking oil (b) 5-LDH derived FAME (c) 10-K^+/LDH derived FAME.

4.3 CATALYTIC ACTIVITY

Among the various amount of catalyst 5wt% gives maximum yield. 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 (a) Effect of impregnated K^+ concentrations on LDH (b) amount of catalyst with respect to oil (c) methanol to oil molar ratio and (d) reaction temperature. The reusability of catalyst also studied.

4.3.1 Effect of impregnated K^+ concentrations in LDH

To determine the optimal amount of potassium impregnation on LDH, a series of catalysts were prepared by varying the amount of potassium ion from 2-10wt% on LDH. The transesterification of waste cooking oil was performed with methanol to oil molar ratio of 9:1 at 65°C in the presence of 5wt% of the prepared catalysts with respect to oil and for reaction duration of 2.5 h. **Fig 11** suggests that up to 10wt% increase in the K^+ concentration was found to enhance the activity of the K^+/LDH catalyst. However, further increase in the K^+ concentrations has not influenced activity of K^+/LDH on transesterification of waste cooking oil. The increase in

activity may be due to the increase in active site on increasing the K loading in LDH. Hence, for further study 10-K^+/LDH was selected for optimizing the other reaction parameters.

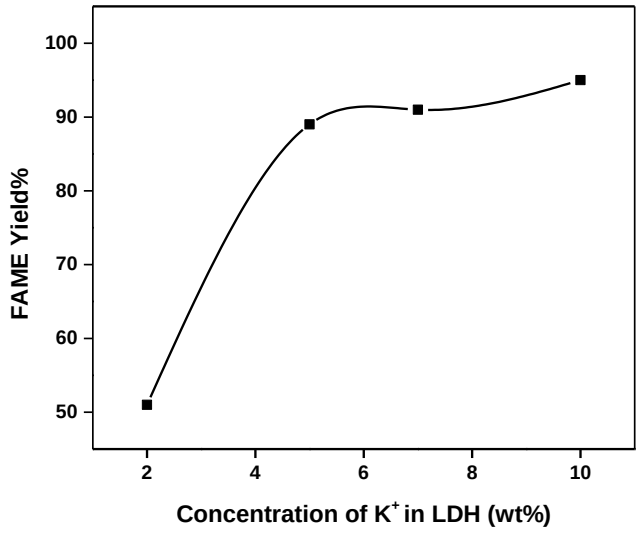


Fig 11. Effect of K^+ concentrations in LDH on the FAME (reaction conditions: methanol/WCO molar ratio 9:1, catalyst amount-5wt% with respect to oil, temperature – 65°C, and reaction duration 2.5 h).

4.3.2 (a) Effect of catalyst amount on transesterification activity

In order to determine the optimum catalyst concentration, a series of transesterification reactions of waste cooking oil with methanol was performed in presence of 10-K^+/LDH employing methanol/oil molar ratio of 9:1 for 2.5 h and varying the catalyst concentration 5-10wt% (with respect to oil). The best yield of FAME is given by 5-10-K^+/LDH catalyst as shown in **Fig 12a**. (10 represent K loading on LDH and 5 represents catalyst amount in wt% taken for reaction). The fame yield was found to decrease with the increase in catalyst amount. This could be due to the fact that at higher catalyst loading reaction mixture becomes more viscous which could repel the mass transfer in liquid-liquid-solid system (Wang *et.al.*, **2011**).

(b) Effect of methanol to oil molar ratio on transesterification activity

The effect of methanol/oil molar ratio on transesterification process 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 complete conversion of oil to FAME. To optimize the methanol to oil molar ratio for 10-K^+/LDH catalyst, the reactions were performed by varying

methanol/oil molar ratio from 5:1 to 15:1 for 2.5 h at 65°C. The FAME yield increases from 53% to 97% on increasing methanol/oil molar ratio from 5:1 to 9:1 and further increase in molar ratio was not found to influence FAME yield significantly as shown in **Fig 12b**.

(c) Effect of reaction temperature on transesterification activity

Heterogeneous catalyst, because of phase difference from reagents, usually required a high temperature and pressure and longer reaction time to give the significant conversion. To optimize reaction temperature, the transesterification of waste cooking oil with methanol to oil molar ratio of 9:1, 5wt% of 10-K^+/LDH with respect to oil was carried out at different temperature. The FAME yield increases regularly as the reaction temperature was increased from 35°C to 65°C as shown in **Fig 12c**. From this it was found that reaction is more effective at 65°C.

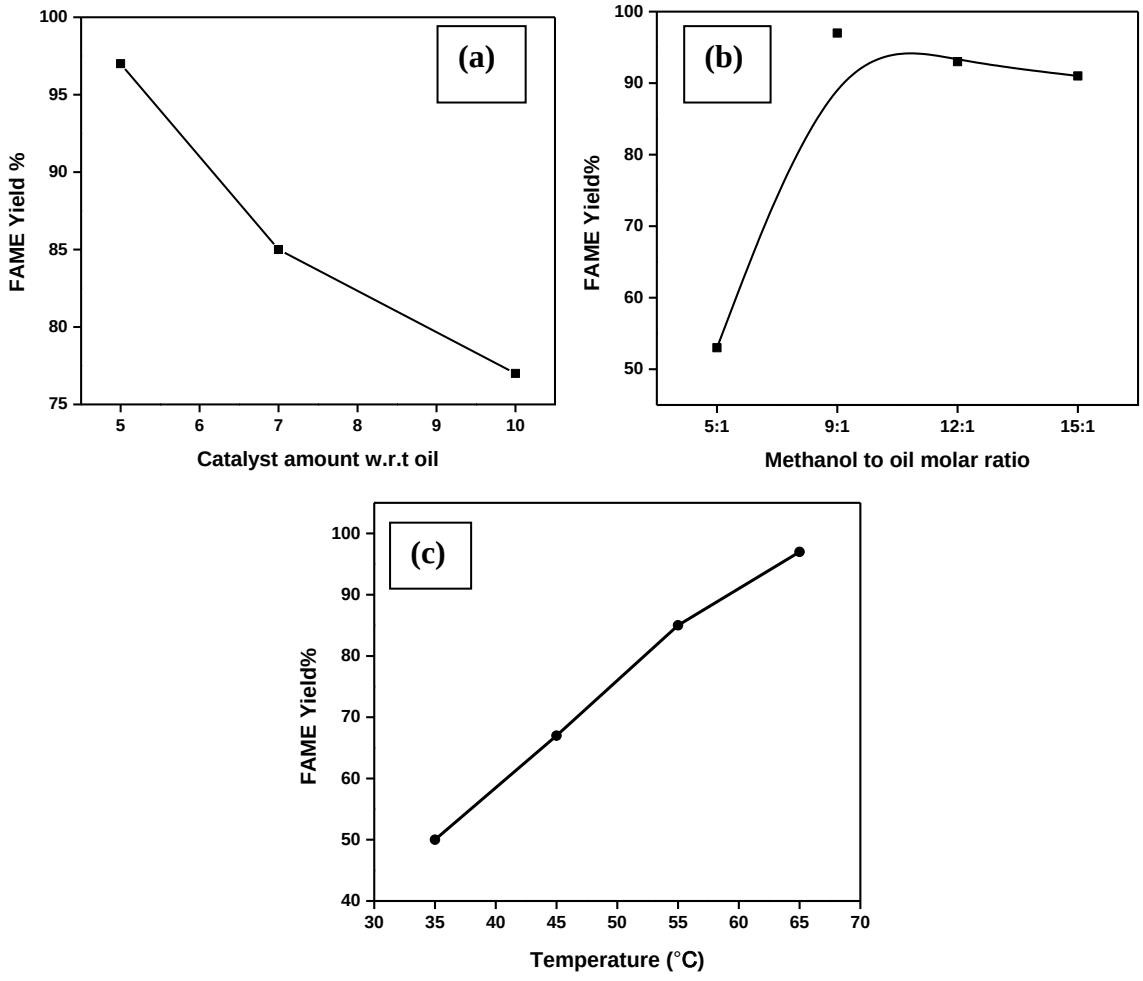


Fig 12. (a) Effect of catalyst amount with respect to oil, (b) Effect of methanol to oil molar ratio and (c) Effect of reaction temperature on transesterification activity.

- Thus, a 9:1 methanol to oil molar ratio at 65°C in presence of 5wt% catalyst (with respect to oil), was found to be an optimum condition for 10-5-K^+/LDH-550°C catalyzed transesterification of waste cooking oil.

4.3.3 Homogeneous contribution study

Transesterification reaction was carried out with 1 g of K^+/LDH catalyst (5wt%) in methanol/oil molar ratio (9:1) at 65°C in a round bottom flask for 1 h. The reaction mixture was allowed to cool and the filtrate was collected. After this the reaction was continued using the filtrate and reaction was continued for another 1.5 h and the yield after every 30 min was analyzed by proton NMR technique. In absence of catalyst no further increase in FAME yield was observed as shown in **Fig 13**, to support that that there is no homogeneous contribution involved in catalytic activity.

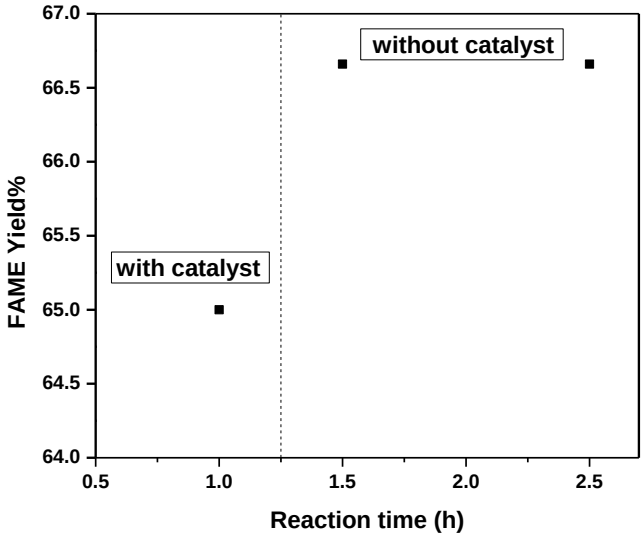


Fig 13. Plot showing homogeneous contribution study of transesterification reaction (reaction conditions: catalyst amount- 5wt%, methanol/oil molar ratio-9:1, temperature 65°C).

4.3.4 Reusability Study

The reusability of heterogeneous catalyst is a big advantage over homogeneous catalyst because it reduces the overall processing cost of the reaction. To test the reusability of x-K^+/LDH, transesterification of the waste cooking oil was performed with methanol under optimized reaction conditions. After completion of reaction, K^+/LDH catalyst was recovered from the reaction mixture by centrifugation and then washed with hexane, dried at 120°C for 12 h and

then finally calcined at 550°C for 4 h. The catalyst thus recovered and regenerated was employed for 4 successive catalytic cycles under same experimental and regeneration conditions. As shown in **Fig 14**, the reused catalyst was also found to yield >90% FAME yield in two successive catalytic runs and in third run the FAME yield falls up to 66% and required 5 h for the completion of the reaction. However, in fourth cycle only 43% conversion was achieved even after 7.5 h of reaction. The gradual loss in 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 sites from the catalyst.

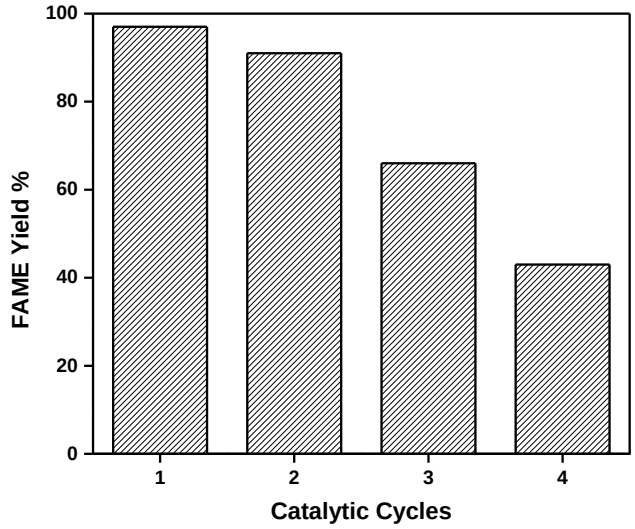


Fig 14. Reusability studies of K^+/LDH catalyst transesterification of waste cooking oil showing FAME yield (reaction conditions: methanol/oil molar ratio-9:1, catalyst amount- 5wt% with respect to oil, temperature 65°C and reaction duration 2.5-7.5 h).

The powder XRD pattern of reused K^+/LDH catalyst show new peaks at 2θ = 28.8°, 30.5°, 31.8° due to the formation of a new hexagonal-phase of K_6MgO_4 (JCPDS card no. 01-070-1176) and at 2θ = 35°, 51°, 59.7°, 62.4°, 65.5°, 67.4°due to the hexagonal-phase of K_2O (JCPDS card no. 00-026-1327). While the peaks corresponding to the cubic phases of $Mg(OH)_2$ and hexagonal phases of AlO(OH) were no longer found in the XRD patterns of reused catalyst. Thus structural changes in the catalyst are primarily responsible for the loss of catalytic activity.

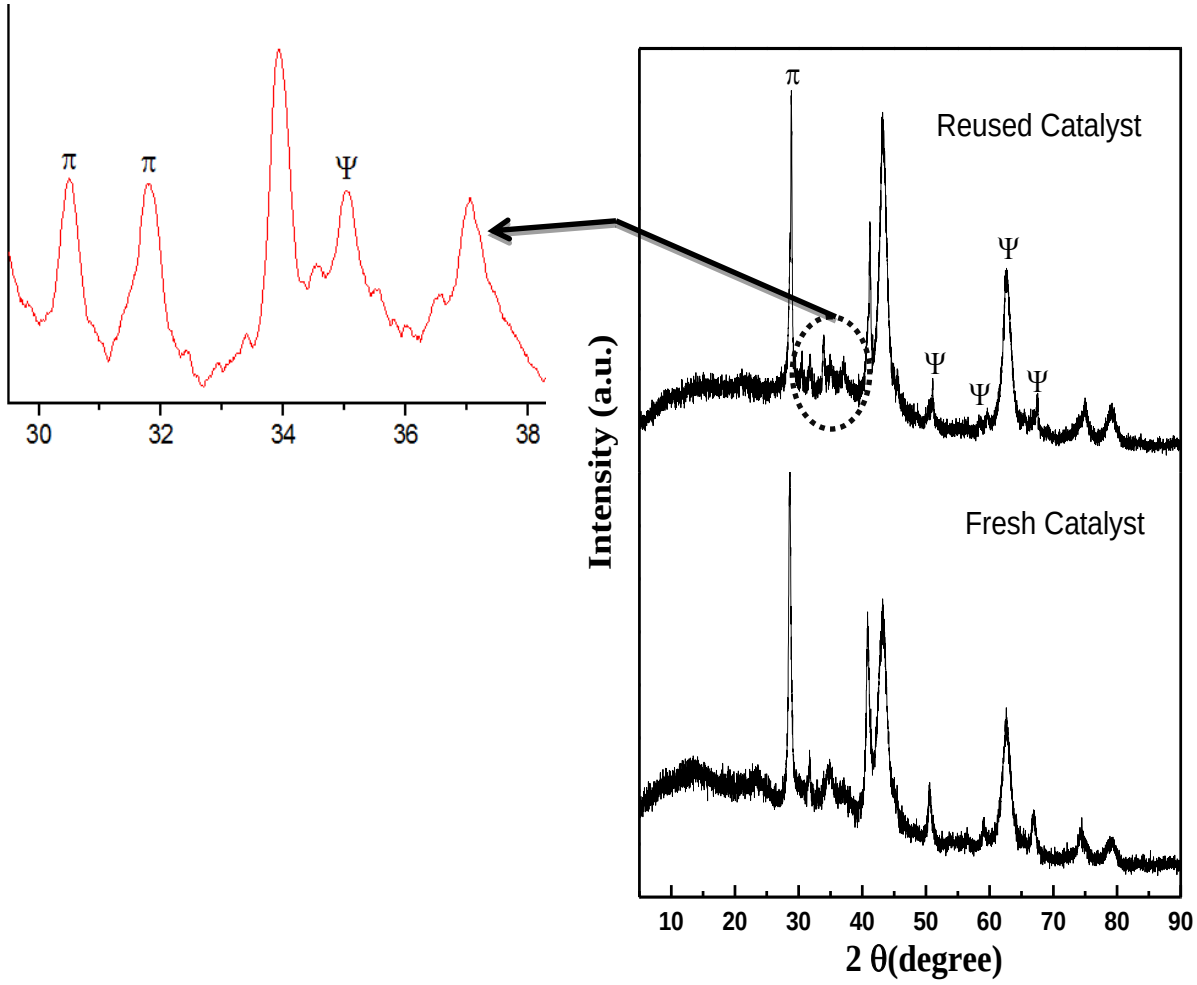


Fig 15. XRD pattern of fresh catalyst and reused catalyst. ($\psi = K_6MgO_4, \pi = K_2O$)

4.4 KINETIC STUDY

To study the kinetics of transesterification reaction was performed under optimized reaction condition and the samples from the reaction mixture were taken out after every 30 minutes and subjected to ^{1}H NMR analysis to quantify the FAME yield. The conversion of WCO at different reaction duration was obtained and fitted in zero order (equation 1), first order (equation 2) and second order (equation 3) kinetic models,

$$\frac{Kt}{100} = X_{me} \text{---------- (1)}$$

$$\mathbf{ln}(\mathbf{1} - \boldsymbol{X_{me}}) = \boldsymbol{kt} \text{ ---------- (2)}$$

$$\mathbf{100}\boldsymbol{kt} = \frac{\boldsymbol{X_{me}}}{\mathbf{1}-\boldsymbol{X_{me}}} \text{ ---------- (3)}$$

where, k is rate constant (min^-) and t is time (min).

As could be seen from **Fig 16**, linear fitting was obtained when data was fitted with first order kinetic equation. This supports that under the given experimental condition K^+/LDH catalyzed transesterification reaction has followed the pseudo first order kinetics. Most likely reaction rate is independent to the alcohol concentration as it is used in excess to the oil.

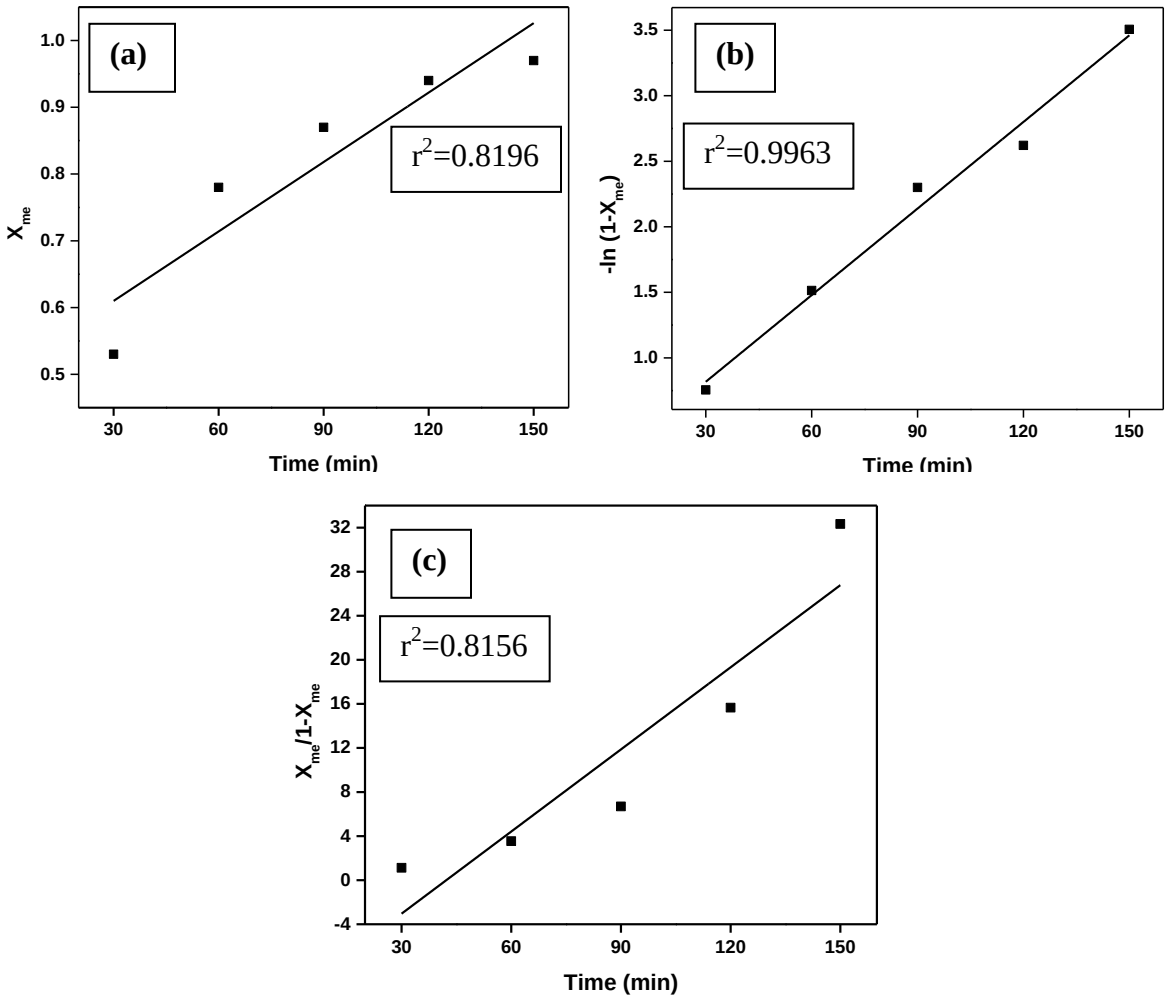


Fig 16. Plots of (a) Zero order reaction (X_{me} versus time), (b) 1st order reaction (-ln(1-X_{me})versus time) and (c) 2nd order reaction (X_{me}/1-X_{me} versus time) [reaction conditions: methanol/oil molar ratio-9:1, catalyst amount- 5wt% with respect to oil and temperature 65°C].

CHAPTER 5

CONCLUSION

In present study the transesterification of waste cottonseed oil with methanol were studied in presence of K^+/LDH as heterogeneous catalysts. The physico-chemical properties of the catalysts were evaluated by powder XRD, SEM-EDS and Mapping, TGA, and FT-IR studies. The effects of parameters such as methanol/oil molar ratio, reaction temperature and catalyst amount with respect to oil were investigated. Under optimized reaction conditions of 9:1 methanol/oil molar ratio, 65°C reaction temperature, low catalyst loadings (5wt%), and 2.5 h reaction duration > 97% FAME yield was obtained. The K^+/LDH heterogeneous base catalysts showed good activity compared to the bare LDH. The transesterification reaction was found to follow pseudo-first order rate law. Further, the catalyst could be reused during four catalytic cycles however, after two runs the FAME yield was found to reduce.

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