

**POTASSIUM BASED CALCIUM OXIDE  
CATALYST SYNTHESIS FOR EFFICIENT  
TRANSESTERIFICATION OF WASTE  
COOKING OIL**



**By**

**Bushra Hassan**

**206368**

**Session 2017-19**

**Supervised by**

**Dr. Rabia Liaquat**

**A Thesis Submitted to the U.S.-Pakistan Center for  
Advanced Studies in Energy in partial fulfillment of the  
requirements for the degree of  
MASTER of SCIENCE in  
THERMAL ENERGY ENGINEERING**

**US-Pakistan Center for Advanced Studies in Energy (USPCAS-E)  
National University of Sciences and Technology (NUST)  
H-12, Islamabad 44000, Pakistan  
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August, 2021**

# THESIS ACCEPTANCE CERTIFICATE

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## DEDICATION:

I want to dedicate my thesis to my husband Nashit, and my parents Khalida and Hassan.

## **ACKNOWLEDGEMENTS:**

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Finally, I am extremely thankful to NUST for helping me with their financial assistance through a merit-based ICT Endowment scholarship.

Thank you

Bushra Hassan

## ABSTRACT

Waste cooking oil conversion to biodiesel is indeed an efficient and environment-friendly way to overcome environmental pollution and energy crisis owing to nontoxic nature of Biodiesel synthesized by Heterogeneous Catalyst (K-CaO). Utilization of waste cooking oil participates both in reducing the overall greenhouse gas emissions to minimum level and further in obtaining economical biodiesel. During synthesis, the crushed waste eggshells were calcined in muffle furnace at 950°C, for 3 hours. CaO were impregnated with Potassium i.e K-(CaO) for transesterification. The catalyzed reaction was proven to be most efficient with molar ratio of 12:1 and temperature 60°C in the presence of 7% catalyst. The biodiesel yield from transesterification was approximately 92% of Fatty Acid Methyl Ester (FAME) produced in an hour. Furthermore, the catalytic activity in transesterification of waste cooking oil and its physicochemical properties were examined by Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) and X-Ray Diffraction (XRD). Hence production of the biodiesel from waste cooking oil was proven worthy aided by catalyst K-(CaO) synthesized using waste eggshells.

Keywords:

Transesterification

Waste Egg Shell

Biodiesel

Heterogeneous Catalyst

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## **PUBLICATION:**

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# Chapter 1: INTRODUCTION

## 1.1. BACKGROUND:

The diminishing traditional resources for the fuel production are responsible for increase in diesel price and diesel's toxic nature increases environmental concerns that inspire the diesel fuel replacement. Owing to this, renewable, biodegradable, nontoxic, ecofriendly and free from sulfur and aromatics nature of Biodiesel is found to be more competitive diesel for fuel substitution [1] [2]. Production of biodiesel is feasible by utilizing number of transesterification technologies. Oils and fats (OF) are processed with alcohol (usually methanol) and a catalyst. The reaction breaks and separates out oil molecules (triglycerides) apart and the desired yield i.e. alkyl esters (biodiesel) is obtained with glycerin as a by-product after purification and separation. [3]

Biodiesel is extracted from renewable resources like vegetable oils such as soya beans, palm, sunflower canola, jatropha, rapeseed, cottonseed and animal fats. Using edible oils and animal fats for fuel generation can shorten the food chain, furthermore animal fats have higher amount of saturated fatty acids, so it cannot be the ideal raw material [2]. Selection of the raw material creates high impact on the overall cost for producing biodiesel. Another vegetable oil i.e. Waste cooking oil (WCO) whose considerable quantity is usually dumped into landfills or rivers, which is responsible for land and water pollution. WCO is available all over the world where ever food is cooked so its usage in the biodiesel production is comparatively very economical and environmental friendly than virgin oils, [2] hence, WCO is the promising feedstock in biodiesel production. [3]

Homogenous catalysts are fast and don't require harsh conditions in transesterification reactions but efforts are made on the production of solid (heterogeneous) catalysts because of their reusability, high purity, non-corrosive nature, longer life and easy separation of biodiesel and glycol [1] [3]. Among these catalyst alkaline earth metallic oxides like (CaO, MgO, SrO) have proven worthy because of their higher activities in the process of transesterification. Moreover, CaO is ecofriendly also. There are various feed stocks like



( $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$ ,  $\text{Ca(NO}_3)_2$ ) used for the production of Calcium oxides [2]. Besides these, natural calcium sources like animal shells and bones can be achieved from wastes that will not only reduce catalyst cost but also helpful in waste management. [3]

In this research, initially calcium oxide is prepared from waste eggshells, and then impregnated with the different concentrations of potassium ion to increase basicity of ( $\text{CaO}$ ) alkaline catalyst used for the process of transesterification. Activity of obtained catalyst was tested with different oil to methanol ratio for producing biodiesel, followed by different techniques for analyzing obtained biodiesel properties.

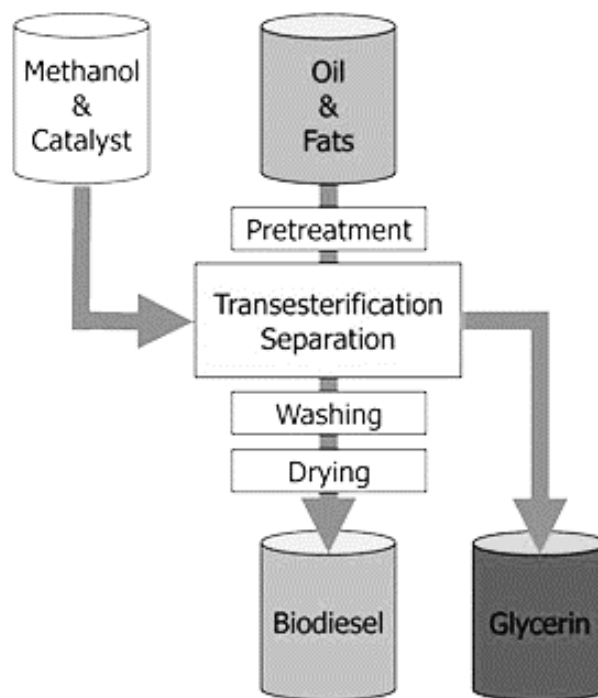


Fig 1.1 Biodiesel Production from Waste Cooking Oil [3]

## **1.2. PROBLEM STATEMENT:**

As increase in world's population, energy demand is also increasing day in day out. Fossil fuels will not be enough to meet high energy demand because of limited reservoirs. To meet such high demand biofuels are the best alternatives. Biodiesel can be produced from clean and renewable procedures that's why it will reduce pollution by reducing greenhouse gases emissions.

Various catalysts are used in the process of transesterification but the entire procedure is more expensive than conventional fuels because of high cost of catalyst, in this research catalyst (K-CaO-3.5) is composed of waste egg shells which is economical and efficient.

## **1.3. SCOPE OF THE STUDY:**

1. Environment friendly way to produce diesel
2. Reduce emission of greenhouse gases
3. Enhanced rate of transesterification.
4. Alternate energy source
5. Production of more efficient catalysts from waste

## **1.4. OBJECTIVES OF THE STUDY:**

1. To synthesize K-CaO (composite heterogeneous catalyst from waste egg-shells)
2. Production of Biodiesel (Fatty Acid Alkyl Ester) from waste cooking oil

## **1.5. SUMMARY:**

Form the past few decades there is an increase in harnessing energy from renewable resources to meet the energy demands because conventional sources of energy have proven to be the culprits of environmental deterioration. Focus is also being given on novel energy means which are more efficient and less polluting. Biodiesel is one such example which is such an energy carrier that it can be produced by multiple methods This research has important applications in the field of waste to energy as it can enhance the

Biodiesel production from catalyst synthesis which can be used for energy applications.  
This chapter presents the aims and objectives of this thesis.

# References

- [1] D. S. K. K. J. S. A.Kumar, *Res. Eng*, vol. 1, p. 57–62, 2014.
- [2] P. B. G. Lourinho, *Rev. Environ, Sci. Biotechnol*, vol. 14 , p. 287–316, 2015.
- [3] S. T. T. M. J. C. K. U. S. K. A. Y. T. K. S. S. K. Urasaki, *Appl. Catal., A* , vol. 44, pp. 411-412, 2012.

# CHAPTER 2: LITERATURE REVIEW

## 2.1. BIODIESEL BACKGROUND:

The current perspective of research in the field of biodiesel production targets on the production of biofuels as second generation with substrates like non edible plants /foods and waste vegetable oil. GOP discharged the tax and custom duty charges from the import of any utility required for biodiesel production such as plant, machinery. equipment and other items to help Economic Coordination Committee (ECC) of the cabinet to execute their decision of research and development in this field. Pakistan State Oil (PSO) company started its working to meet the deadline of 10% share of biodiesel by 2025 for which it selected non-edible plants/seeds species, such as castor. Jatropha, jojoba etc., for production of biodiesel. In Pakistan, the Alternative Energy Development Board (AEDB) also launched biofuel initiatives. [3] [8] [9]

Biodiesel is a renewable fuel alternate which can be formed by chemical combinational with an alcohol and any oil or fat. For producing Biodiesel industrially, methanol is widely used as a feed stock. [6] [2] Alcohol is abundantly derived from sugarcane and synthesis of natural gas. Pakistan is a rich land full of natural species and agricultural equity where 70% population works in farm fields and the soil survey classified into 79 types of soil throughout the country. [10] [6] More than 80 million acres of land which is of deprived quality and is best for cultivation of energy crops in Pakistan so this is a practical consideration for bioenergy production [3] [7]

Biodiesel can be formed using already developed agricultural practices but 60% population located in rural areas utilize conventional methods like woods and organic waste (animal and crop residue) for domestic needs as they are unable to access commercial energy. [11] [12] [2]

Biodiesel is normally formed by oils, fats, or other types of biomass. In Europe biodiesel is commonly composed from mustard oil. The production of biodiesel is much less toxic than oil petroleum diesel the emissions from conventional diesel have around 79% highly

toxic pollutants including inorganic and organic components which are not only dangerous for the environment (global warming, greenhouse gas emissions and smog formation) but for the health being carcinogenic and mutagenic such as sulfur oxide, nitrogen oxide and particulate matter. Almost 21 distillery units around the country sufficient to process around 2 million tons of the molasses producing 400.000 tons of bioethanol are the main source of alcohol production from sugar cane though it exceeds the country's needs plus export by 318,000 tons. Thus we have sufficiently excess stock of alcohol for the process of transesterification for biodiesel production. [13] [5] [8]

Biodiesel may be used in a pure form (B100) or blended with petro-diesel in B2, B5, B20 and B100 (pure). Biodiesel has helped various countries in minimizing their reliance on foreign oil reserves as it produced domestically and can be used with or without change to the engine and fuel system in diesel engines. biodiesel after cultivating all the uncultured land around while the current requirement is nearly 8.5 million tons though a 10% increase of energy is expected per year. Hence biodiesel has an encouraging future in Pakistan owing to raw materials' availability and certain energy generation programs

**2.1.2. COMPARISON BETWEEN BIODIESEL AND FOSSIL DIESEL:**

<b>BIODIESEL</b>	<b>FOSSIL DIESEL</b>
Nontoxic	Toxic.
higher lubrication	Lower lubrication
Renewable	Non renewable
No gasses emission	toxic gasses emission e.g. CO <sub>2</sub> , NO <sub>x</sub> , SO <sub>x</sub>
Biodegradable	Non-biodegradable
high flash point	Low flash point.
Combustion efficiency increases due to high cetane number	Low octane or cetane number
anti-freezing additive in cold weather are required due to its higher density.	anti-freezing additive in cold weather are lesser required due to its lower density

Table 2.1 Comparison between Biodiesel and Fossil Diesel [13]

## **2.2. SOURCES OF BIO-DIESEL**

The feed stock for biodiesel production are abundant and can be used. The main sources of this product are plants. The feed stock for any bio-diesel may be categorized depending on availability and production, in oil crops, wild oil, yielding trees, microorganisms, animals and other biotic byproducts. [9] [8]

Biodiesel can also be formed from waste vegetable oil and animal fats. Animal fat can be used to produce Biodiesel but this is rarely used due to paucity in supply of animal fat [7] [3].

Various feed stocks are used in biodiesel production some of them are given below:

- Virgin oil feedstock
- Waste vegetable oil
- Animal fats including lard, yellow grease, tallow, chicken fat and the by-products for the production of Omega-3 fatty acids from fish oil.
- Algae
- Oil from halophytes
- Sewage Sludge

Due to the short comings regarding source of raw material for the biodiesel production, non-edible domain is gaining focus. Researchers suggested that non edible oils like waste cooking oil are best for the process of transesterification [8] [7]

### **2.2.1.WASTE COOKING OIL AS VIABLE SOURCE:**

Currently, there is a high conflict on food chain. For this reasons, the cost of raw materials is reduced through using economical waste cooking or non-edible oils. The most cost-effective and economical production of biodiesel is by using waste cooking oil. Because

feed stock prices are one of the main issue concerning the production of biodiesel, the use of WCO significantly improves the financial viability of biodiesel production

Since large quantity of WCO are illegally dumped in landfills and waterways causing pollution in the environment, the use of WCO to generate biodiesel a replacement for petro diesel provides significant benefits due to reduced pollution. The production of biodiesel from WCO for diesel substitutes is particularly crucial due to the declining trend in global oil reserves, environmental issues created using fossil fuels and the inflated prices of petroleum products on the global market. [8] [3]

Unfortunately, a significant free content of fats reduces the operation of the catalyst that reduces the yield of biodiesel. Therefore, an effective purification esterification of the biodiesel generated must be carried out with acid-catalyzed as the best approaches of free fatty acid. The use of high FFA oils in conjunction with the alkaline-catalytic transesterification can be an excellent method of biodiesel production. Researchers suggest that best source of biodiesel is vegetable oil. [11] [2]

### **2.3. BIODIESEL PRODUCTION METHODS:**

Biodiesel is an easily degradable and nontoxic fuel, free of exhaust gases in the comparison to conventional diesel fuel. The esterification and transesterification reactions from animal fats or vegetable oils in the presence of alcohols and acid or base catalyst are implied for biodiesel production. [1] [5] There is an extensive range of homogenous and heterogeneous catalysts which is utilized for the synthesis of biodiesel such as acidic, basic or enzymatic etc. Chemically, molecules of biodiesel are mono-alkyl esters generally generated from esters of triglycerides. Oils and fats are pretreated to remove water and impurities. With the use of special pretreatment techniques (esterification), free fatty acids can be eliminated or converted into biodiesel. The processed oils and fats then combined with an alcohol and an alkaline catalyst, triglycerides are extracted and converted into alkyl esters and glycerin, which are then isolated from each other and purified. [6] [3]



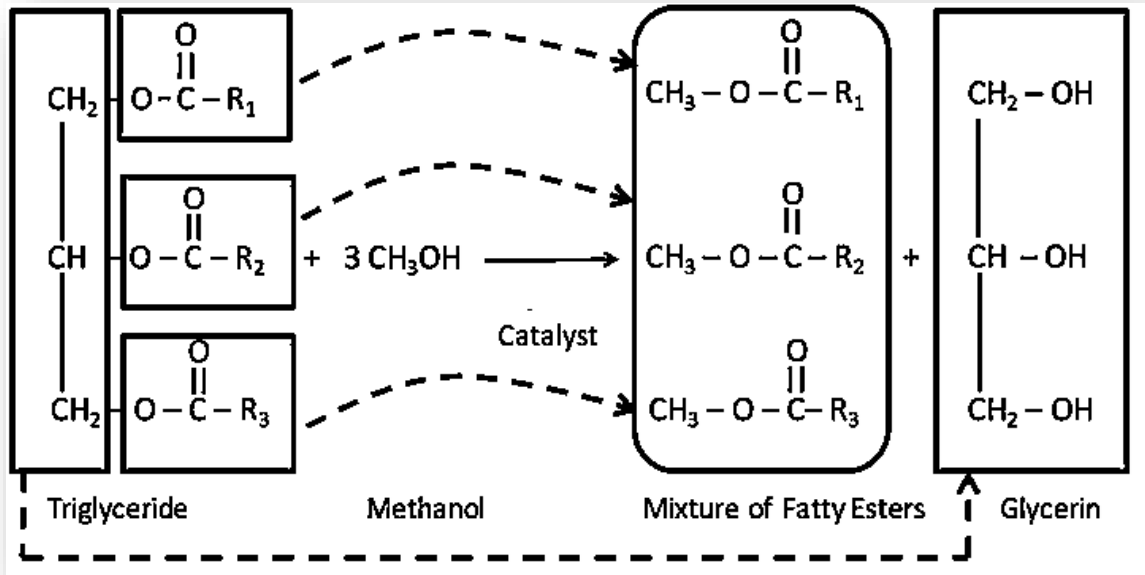


Fig.2.1. Chemical Reaction of Transesterification [2]

### 2.3.1.ESTERIFICATION:

Carboxylic acid reacts with alcohol in the presence of an acid catalyst produce ester along with water as a byproduct. The reaction is called the Fischer esterification.

Reaction of carboxylic acid with alcohol to make an ester (Fischer esterification)

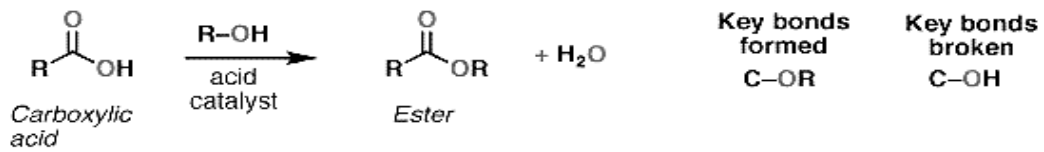


Fig.2.2. Esterification [5] [2]

### 2.3.1.1. MECHANISM:

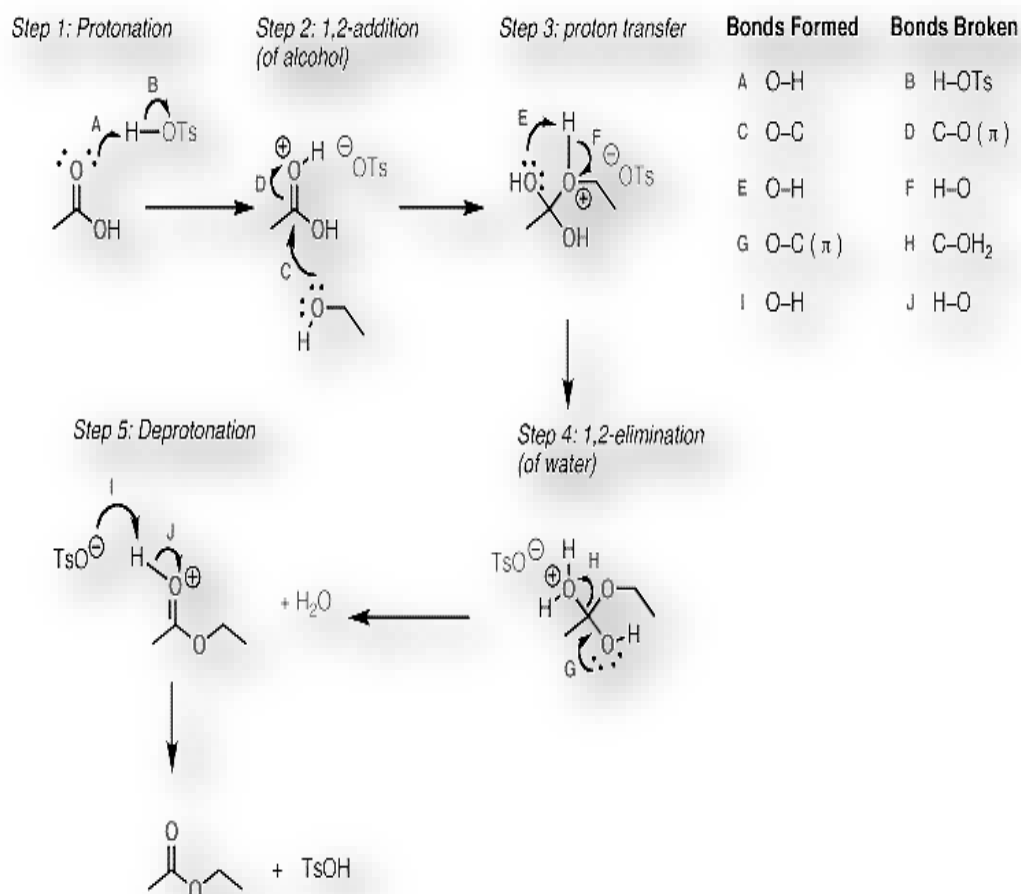


Fig.2.3. Mechanism of Esterification [2]

### 2.3.2. TRANSESTERIFICATION:

The transformation of a carboxylic acid ester into multiple carboxylic acid esters can be termed as Transesterification. [8] [7]



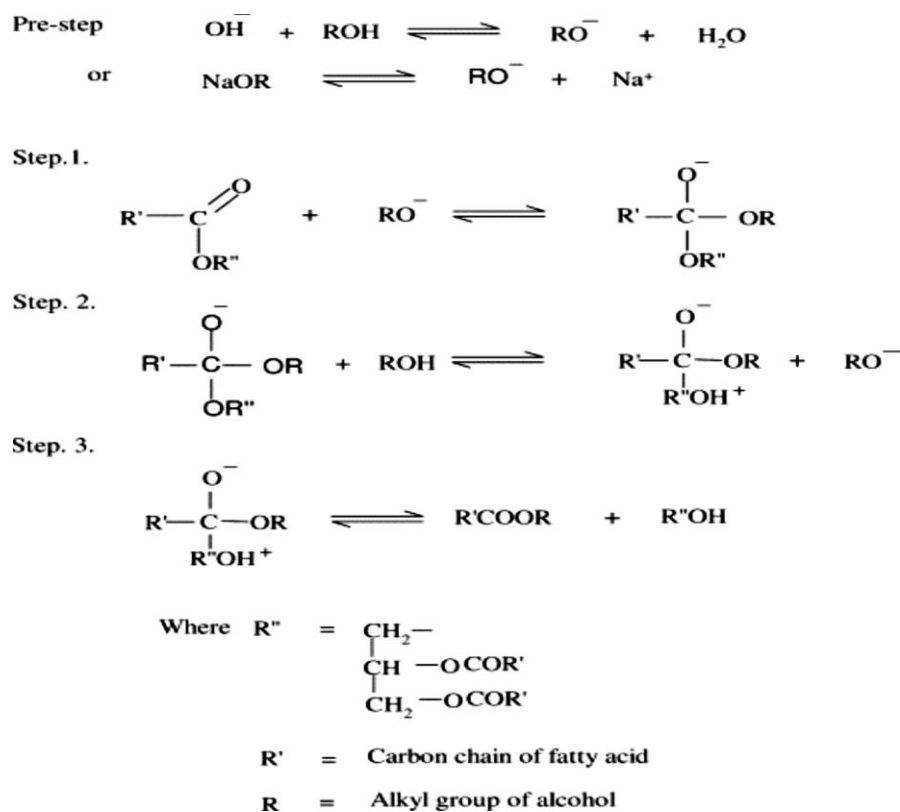


Fig. 2.5 Mechanism of Transesterification [2]

## 2.4. CATALYST SYNTHESIS FOR BIODIESEL PRODUCTION:

Normally, a catalyst is used to enhance reaction speed and yield. Catalyst is the substance that accelerates a chemical reaction without itself being affected. It will provide the site to reactants to be activated and interacted together [9] [7]

Three catalysts forms are currently used i.e. homogenous, heterogeneous and enzyme processing of biodiesel depending the conditions used in the method. WCO is reacted with alcohol due to improved effectiveness. methanol is used in most instances, Ethanol and isopropyl alcohol, however can also be used in animal fats. [3] [6]

Various factors such as: thermal stability, deactivation and conversion rate interact for the catalyst interface with the selection of the catalyst. Basic-catalytic transesterification is

comparatively quicker than the one with acid, and is the most widespread and commercial technology used today in the most production of biodiesel, which is mainly made from several homogeneous catalysts. The reaction is activated by a stable homogeneous or heterogeneous catalyst. [2] [7]

A number of researches are conducted on catalysts used to convert waste cooking oil into biodiesel. In following tables few catalysts are discussed. [13]

Catalyst	Oil and Fats used	Reaction conditions			Yield
		Temperature (°C)	Reaction Time (h)	Alcohol to Oil Ratio	
Zinc doped Calcium Oxide	WCO				75%
KOH	WCO	64	3	3:1	94%
K <sub>2</sub> CO <sub>3</sub>	WCO	65	3	9:1	97%
CaO/SiO <sub>2</sub>	WCO	60	8	16:1	86%

Table. 2.2 Different Catalysts used to convert WCO into FAME [1] [13]

### **2.4.1. HOMOGENEOUS CATALYSTS:**

Homogeneous catalysts are found at the same phase as reactant used. There has been notable work done on the transesterification of vegetable oils with homogeneous acid and base catalysts like KOH, NaOH, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, CH<sub>3</sub>ONa etc. Homogeneous catalysts are found more efficient than heterogeneous and can be easily handled because of the same phase of reactant. It is difficult to handle a different phase catalyst or heterogeneous catalyst, but homogeneous catalysts cause the problem of intoxication and saponification due to higher acid value. With rapeseed oil and soybean oil with high FFA feedstock the homogeneous acid catalyst can be used. [8] [10]

#### **2.4.1.1 DRAWBACKS FOR HOMOGENEOUS CATALYSTS:**

Homogeneous processes of base transesterification have several disadvantages because of their complexity in biodiesel purification process. It can be a major problem if soap is produced due to the existence of huge quantities of free fatty acids in vegetable oil during transesterification. Small quantity of catalyst is used for soap formation and which decreases the catalytic efficiency. In addition, huge amount of waste water is produced during biodiesel purification or washing for the removal of residual catalyst. Finally, the catalysts used cannot be recovered and assisted by the biodiesel system process. [1] [3]

### **2.4.2 HETEROGENEOUS CATALYSTS:**

Heterogeneous catalysts are emerging to seek great attention due to their reusable and noncorrosive nature carrying out transesterification and esterification reaction having acid and base both. It is easy to extract heterogeneous catalysts from biodiesel without producing wastewater, as opposed to homogeneous catalysts. [9] [10] Use of heterogeneous catalysts is efficient and continuous process that could be built and improves biodiesel production economics. In addition, however, the transesterification levels of the active sites of a solid catalytic, that is connected to the three-phase process (oil-methanol-solid catalyst), are generally lower than those of the homogeneous catalyst. Often, active species of most heterogeneous base catalysts leach in the reaction mix and create soap where are free fatty acids (FFAs) containing vegetable oil. The deterioration

of solid-base catalysts restricts the probability of reuse or for longer use during a continuous cycle in subsequent batches. It must also be remembered that solid base catalysts are primarily active at the temperature around the boiling point of methanol in transesterification. In view of the above remarks, emphasis has been on enhancing catalytic activity and stability of solid catalysts with regard to current research and development of heterogeneously catalyzed biodiesel. [2] [10] The common problems caused by the use of heterogeneous catalysts e.g. mass transfer resistance, fast deactivation, time consumption and inefficiency; can be resolved by

There are several reported examples of heterogeneous catalysts as metal oxides, mixed metal oxides, alkali doped metal oxides and transition metal oxides etc.

#### **2.4.2.1 CALCIUM OXIDE DERIVED CATALYST:**

Natural waste shell catalyst or single metal oxide heterogeneous based catalysts is probably the most studied methods for the generation of biodiesel due to availability, cost and high activity. Calcium based catalyst is preferable due to high activity, accessibility and low price

For enhancing CaO basicity, impregnated commercial CaO with aqueous solution of potassium nitrate is reacted, after preparation, the solution was calcined at 575°C and 800°C, for 5 h. To do transesterification, tests were realized at 60 C a 7% of catalyst with 12:1 methanol to oil ratio for 50 minutes. the procedure was always followed with fresh catalysts resulted in biodiesel yields 92%. while, the K-doped CaO catalyst does faster deactivation then the pure CaO. These results disclosed a drawback of the catalyst stability of K/CaO may be owing to the enhanced formation of calcium di-glyceroxide due to the presence of potassium. [9] [10]

Catalyst	Oil and Fats used	Reaction Conditions			Yield
		Temperature °C	Reaction Time hour	Alcohol to Oil Ratio	
Li/CaO	Sunflower Oil	60	3	14:1	90
CaO/MgO	Rapeseed Oil	64.5	6	18:1	92
CaO/SiO <sub>2</sub>	Corn Oil	60	8	16:1	85.6
CaO/Al <sub>2</sub> O <sub>3</sub>	Palm Oil	65	5	12:1	95
CaO/Al <sub>2</sub> O <sub>3</sub>	Soybean	150	6	9:1	90
CaO/ZnO	Sunflower	60	2	12:1	90
CaO/La <sub>2</sub> O <sub>3</sub>	Jatropha	160	3	25:1	98
Ca(OCH <sub>3</sub> )	Soybean	65	65	1:1	98

Table 2.3 Various CaO based Catalysts Reaction Conditions and Yield [5] [10]



## **2.4.2.2. SELECTED CATALYST**

### **CaO is being used because**

1. CaO will be synthesized from waste egg shells.
2. Non corrosive and environmental friendly.
3. Easy handling, low solubility, high basicity.
4. Highly efficient catalyst for biodiesel production

### **K<sup>+</sup> is being used because**

1. It increases the basic strength of catalyst
2. It decreases the reaction time.

## **COMPOSITES**

1. High stability of catalyst
2. Reusability of catalyst

## **2.5. FACTORS INFLUENCING BIODIESEL YIELD:**

Different parameters were considered in the reaction of transesterification. They highly influenced on biodiesel yield factors that were examined during process are:

- ✓ Methanol to oil ratio
- ✓ Temperature
- ✓ Reaction time
- ✓ Catalyst dose

### **2.5.1.METHANOL TO OIL RATIO:**

The oil-methanol ratio creates high influence on biodiesel yield; different reactions were performed with different ratios using different catalysts. From literature, it is studied that one mole for alcohol esterify one mole of free fatty acids, increasing methanol to oil ratio up to a certain limit enhances the reaction while further increase may decrease the yield because it affects the solubility of glycerin. Alcohol has to recover from the product after reaction to purify the final product. [8] [2]

### **2.5.2.TEMPERATURE:**

Increase in temperature decreases the oil's viscosity which increases the rate of reaction. Various reactions have been developed using a catalyst with various temperature ranges. Literature suggests that the FAME production is increased when temperature is raised until 64°C while the further increase in temperature stops the reaction because alcohol evaporates at 65°C Esterification is temperature specific if temperature exceeds than limit it can cause soap formation. [7] [3] [8]

### **2.5.3.CATALYST DOSE:**

Biodiesel yield was highly effected by catalyst concentration; different reactions were performed by using different catalyst concentration increasing the amount of catalyst up to a certain limit increased the biodiesel yield while incomplete amount of catalyst does not complete transesterification reaction. While it is observed from literature, further increase in catalyst dose caused soap formation which decreased biodiesel yield. Moreover, overdosed catalyst increases the reaction cost. [2] [10]

### **2.5.4.REACTION TIME:**

Various reactions were performed in the range of 1 to 6 hours. The reaction time is found very influencing parameter for maximum biodiesel yield increasing the reaction time increases rate of reaction. It depends upon the quantity of FFA present in the oil, whereas pretreated oil needs lees reaction time. From studies it was found that further increase in

reaction time caused no noteworthy change in biodiesel yield and increases the reaction cost. [5]

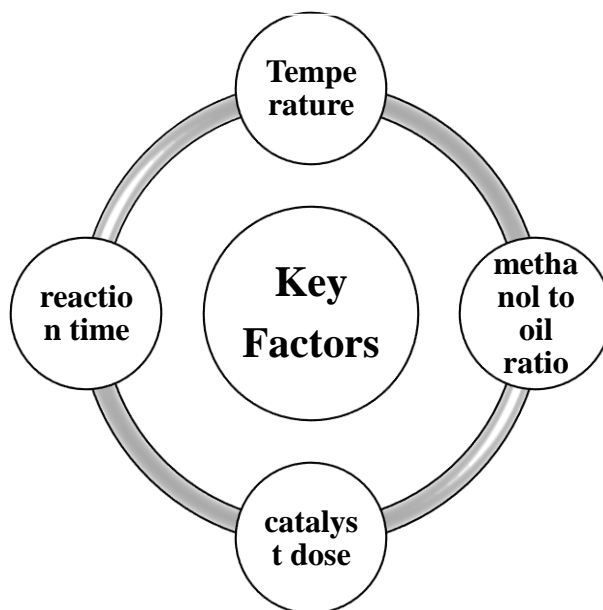


Fig. 2.3. Key Factors affecting Biodiesel Yield [5]

## 2.6. SUMMARY:

Biodiesel production by using K-CaO catalyst is an active research field and utilization of waste as a raw material gives an added advantage of waste to energy conversion. Transesterification is such a process which encompasses waste utilization. This is a complex process which, in the presence of catalyst converts the degradable organic material into methyl ester called Biodiesel. This degradation and transformation is carried out by synthesized catalyst which eventually results in energy recovery as biodiesel production. Many factors govern the success of this process including Methanol to oil ratio, Temperature, Reaction time, catalyst dose, etc. these parameters should be taken into observation in order to get enhance FAME yield.

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# CHAPTER:3 METHODOLOGY:

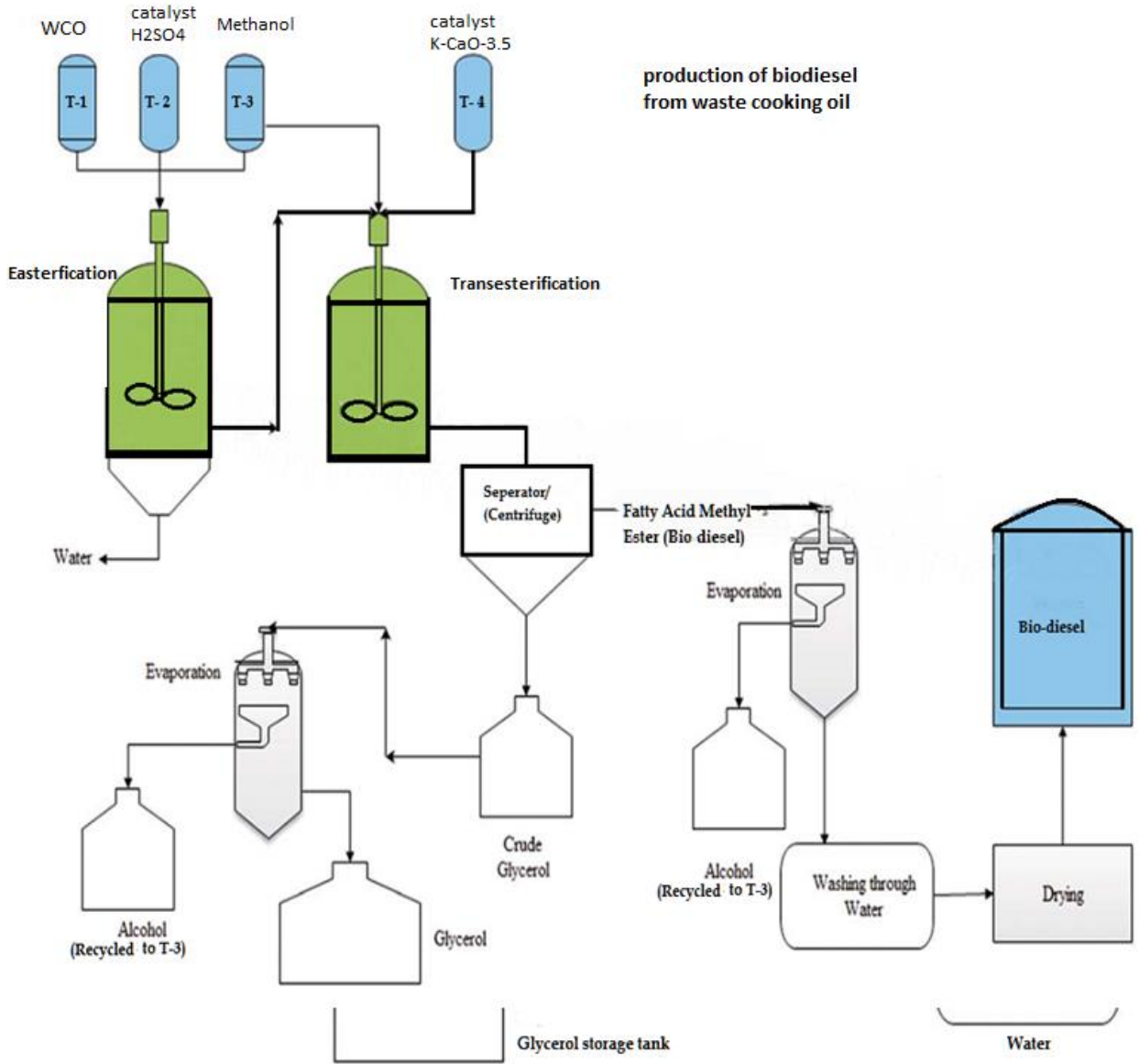


Fig. 3.1 Scheme of Experimental Work

## **3.1. SUBSTRATE SELECTION:**

### **3.1.1. CATALYST SYNTHESIS:**

The feed stock for calcium oxide preparation are abundant. production is abundant The main sources of this product are natural resources like bones and shells. The raw material may be categorized depending on availability and production

Calcium oxide can be synthesized by bones and shells

Different feed stocks are used in calcium oxide preparation some of them are:

- Sea shells
- Lime stones
- Animal bones
- Animal teethes
- Waste egg shells

#### **3.1.1.1. OPTIMUM FEED STOCK:**

Waste egg shells are the most economical and enriched source of calcium that can be find anywhere egg shell is consist of calcium carbonates and proteins and other organic compounds

$\text{CaCO}_3$  can be easily obtained from crushed egg shells and can be converted in  $\text{CaO}$  by the process of calcination.

### **3.1.2. CATALYST APPLICATION:**

The feed stock for biodiesel production are abundant and can be used. The main sources of this product are plants. The feed stock for any bio-diesel may be categorized depending on availability and production, in oil crops, wild oil, yielding trees, microorganisms, animals and other biotic byproducts.

Biodiesel also have formed from waste oil and fats. Animal fat may be used for Biodiesel production but this is rarely used because of the scarcity in animal fat supply.

Various feed stocks are used in biodiesel production some of them are given below:

- Virgin oil feedstock
- Waste cooking oil
- Animal fats including tallow, lard, yellow grease, chicken fat and the by-products of the production of Omega-3 fatty acids from fish oil.
- Algae
- Oil from Halophytes
- Sewage Sludge

### **3.1.2.1. OPTIMUM FEED STOCK:**

Currently, there is a high conflict on food chain. For this reasons, the cost of raw materials is reduced through using economical non-edible oils or waste cooking oils. Unfortunately, a significant free content of fats reduces the operation of the catalyst that reduces the yield of biodiesel. Therefore, an effective purification esterification of the biodiesel generated must be carried out with acid-catalyzed as the best approaches of free fatty acid. The use of high FFA oils in conjunction with the alkaline-catalytic transesterification can be an excellent method of biodiesel production. Researchers suggest that optimum ingredient of biodiesel is vegetable oil.

## **3.2. MATERIAL SAMPLING:**

Waste cooking oil and waste egg shells are collected from university cafeteria and hostel's mess respectively. All chemicals i.e. sulfuric acid ( $H_2SO_4$ ) for esterification, potassium nitrate ( $KNO_3$ ) for catalyst impregnation, methanol ( $CH_3OH$ ) for transesterification were available in university's laboratory

## **3.2. CATALYST SYNTHESIS:**

### **3.2.1. CLEANING:**

Waste egg shells were collected from hostel mess and cleaned from contaminants using distilled water.



### 3.2.2. DRYING:

These cleaned waste egg shells dried at 90°C for 4 hours.

### 3.2.3. CRUSHING:

The dried egg shells were crushed and grinded in grinder to form CaCO<sub>3</sub> powder.

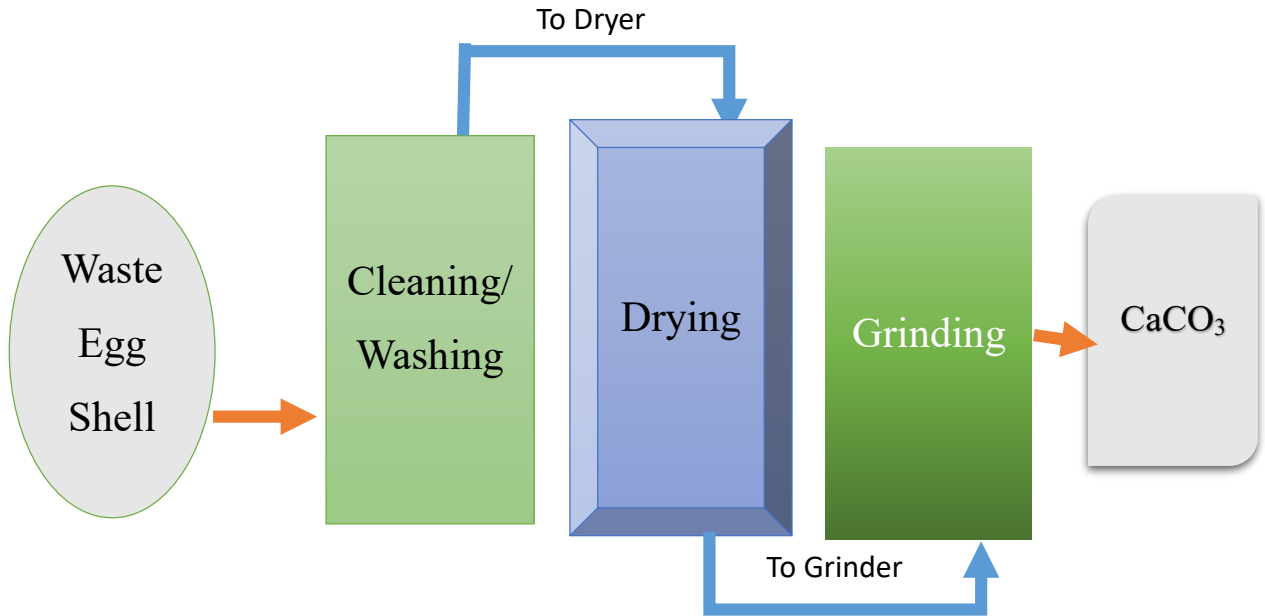


Fig.3.2. Formation of Calcium Carbonate Powder

### 3.2.4. CALCINATION:

The obtained powder then fed to calcination section for 2 hours at 900°C to form Calcium oxide (CaO) [5].

### 3.2.5. WET IMPREGNATION METHOD:

Calcium oxide converted in K-CaO using wet impregnation method. Distilled water (40ml) was used to dissolve 10g of CaO to make a solution initially with 10 ml potassium nitrate aqueous solution with different concentrations was also added to gain potassium ion doped calcium oxide. The obtained mixture was stirred at 500 RPM for 3 hrs at ambient temperature followed by drying 180°C for 24 hours and finally calcined for an hour at 750°C. The obtained catalyst was termed as K-CaO (i.e. 2-4%) [6].



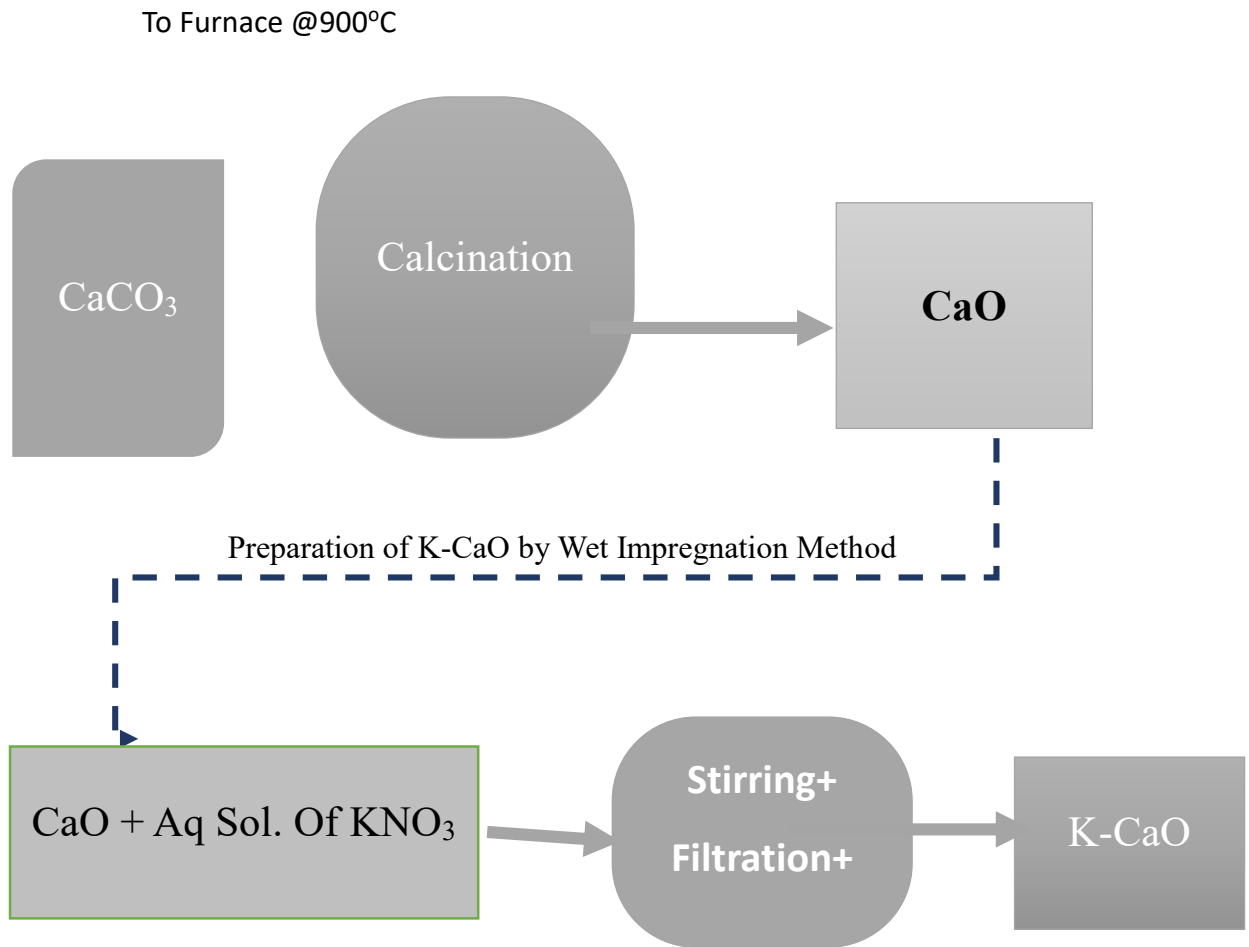


Fig.3.3. Formation of Potassium based Calcium Oxide

### 3.3. PRETREATMENT OF WCO:

#### 3.3.1 FILTRATION:

Initially waste cooking oil (WCO) was collected locally from university's canteen then its pretreatment was performed by preheating and filtration to remove solid food particles.

### 3.3.2 ESTERIFICATION

After that, esterification is performed with acid catalyst i.e. sulfuric acid to remove free fatty acids [7]. In esterification, 25ml of methanol and 2ml of sulfuric acid were mixed with 100ml of waste cooking oil. Afterwards, the mixture poured in a conical flask of 250ml capacity for invariable stirring of the mixture using a magnetic stirrer for an hour. The conical flask was then placed on hot plate at 55°C. After stirring mixture was filtered to separate solid catalyst, then settled for 24 hours, so excess fatty acids can easily be removed. Now the oil is ready for transesterification [8].

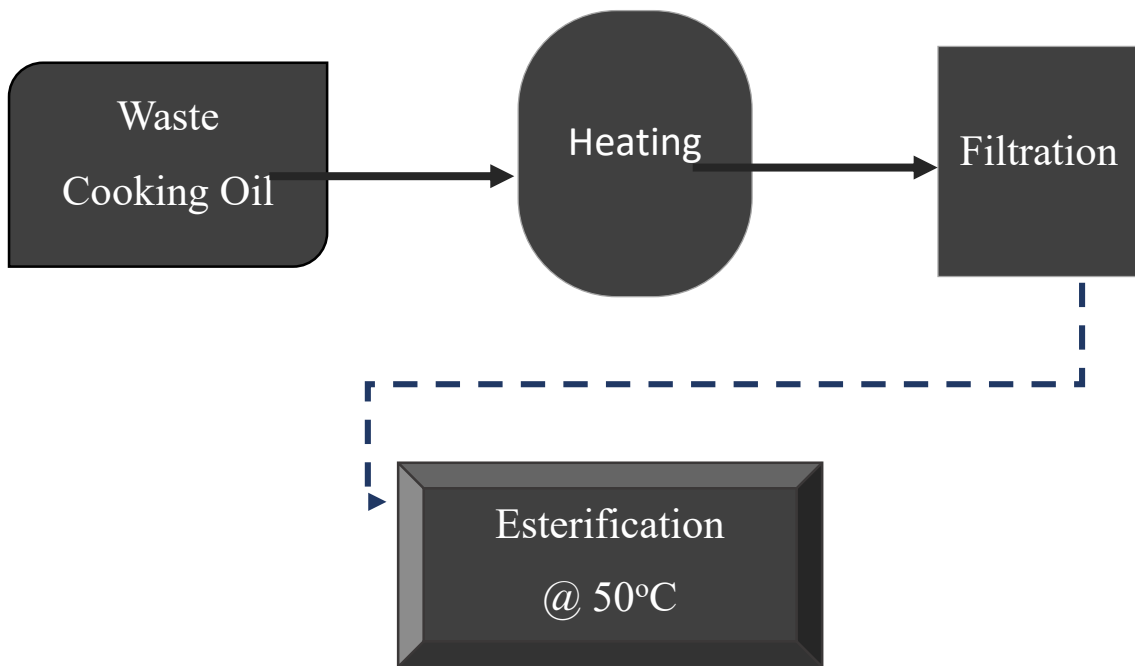


Fig.3.4. Esterification

### 3.4. TRANSESTERIFICATION OF PRETREATED WCO

In this process methanol is processed with waste cooking oil in presence of a catalyst. Mixture of waste cooking oil, methanol and catalyst (K-CaO) preheated at 60°C and then added to pretreated oil. Afterwards, the mixture poured in a conical flask for constant stirring of the mixture using a magnetic stirrer for 60 mins. Transesterification

was carried with different oil to methanol ratio (9:1 to 15:1) and catalyst concentration(1-4% wt). After the continuous stirring for an hour, components of waste cooking oil disintegrated into products. The triglycerides were transformed into methyl esters (biodiesel), then catalyst removed by filtration, methanol by evaporation and glycol is separated by gravity settling. After washing excess methanol was removed and desired biodiesel was obtained. [8]

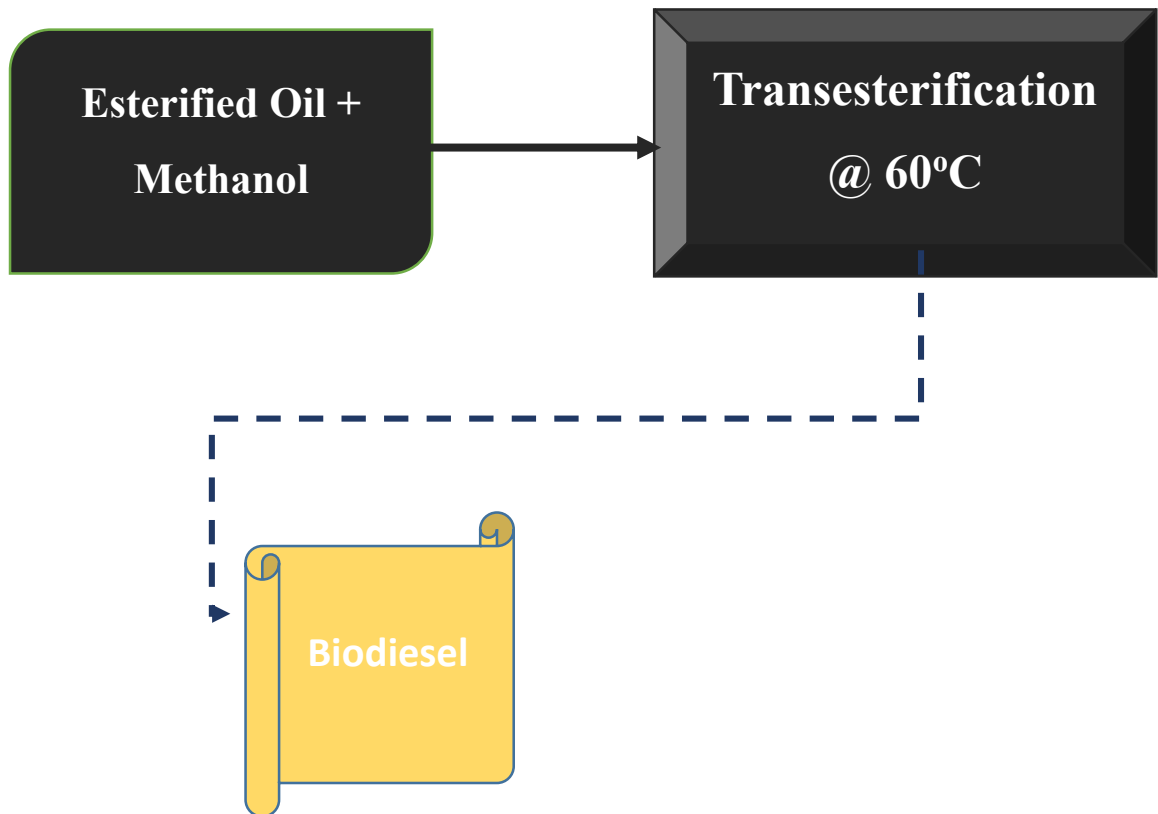


Fig.3.5. Transesterification

### **3.5. CHARACTERIZATION:**

#### **3.5.1. SYNTHESIZED CATALYS CHARACTERIZATION**

For further enhancement in research, solid catalyst i.e. (K-CaO) is characterized by powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer

Emmett Teller (BET) surface area measurement techniques are performed so it can be applied in transesterification of WCO.

### **3.5.1.1. XRD:**

The phase and structure of synthesized catalyst were observed by powder XRD using A Bruker Germany XRD analyzer equipped with Copper as X-ray source with the wavelength of 1.5406 Å catalyst was analyzed at room temperature i.e. (25°C) at an angle of diffraction ( $2\Theta$ ) between 10°C-70°C keeping the step size of 0.02° with time /step was 19 sec [9].

### **3.5.1.2. SEM:**

The morphological characteristics of catalyst were analyzed by Scanning Electron Microscopy (SEM) images by Tescan by cheque Republic; compositional analysis was also performed by using energy dispersive x-ray spectroscopy (EDX) by Oxford instruments, a built-in function of the SEM machine. 10 KV voltage was initially provided to the sample directly mounted on aluminum stubs for imaging [9]. For element analysis, beam energy of 20KV passed through the sample for 2 minutes then the obtained raw data exported to excel for further graphing.

### **3.5.1.3. BET:**

the surface area was calculated by BET using Quanta chrome instruments (USA). For porosity estimation, nitrogen adsorption was performed at highest relative pressure. Before analysis, degassing was carried out at 300°C to clean the surface from volatiles.

## **3.5.2. FAME CHARACTERIZATION:**

Properties of obtained biodiesel were analyzed by different techniques.

### **3.5.2.1. FLASH POINT:**

Biodiesel was accumulated in a vessel whilst it is ignited from the top using a source of ignition. Consequently, rise in temperature of the substance observed from origin to a point where biodiesel produced momentary flash. The temperature measured where flash occurs is termed as flash point.

### **3.5.2.2. VISCOSITY:**

Viscometer was used for the determination of viscosity, probe of viscometer was dipped in biodiesel and heated gently, at different temperatures, different readings of viscosities were noted.

### **3.5.2.3. SOLUBILITY TEST:**

solubility test of biodiesel with methanol was performed to evaluate the amount of unreacted oil in biodiesel. For this test, a mixture of biodiesel and methanol was prepared and shaken for 45 minutes with the help of magnetic stirrer and allowed to settled. After settling, biodiesel was mixed with the methanol. Although a very thin layer of unreacted oil was settled down, that indicates the purity of biodiesel

biodiesel yield was calculated using relation

$$\text{Yield Amountof biodiesel(\%)} = \frac{\text{Amount of biodiesel produced}}{\text{Amountof oil}} \times 100$$

### **3.5.2.4. SAPONIFICATION VALUE**

To determine saponification value of biodiesel, ethanoic solution of KOH was prepared. 0.6 g of potassium hydroxide was dissolved in 0.5 ml of water, then ethanol was added to produce 100 ml. solution was allowed to stand in a tightly-stoppered bottle for 24 hours. 20 ml of this solution was mixed with 0.5g of biodiesel at 40°C, to make a clear solution. An indicator was put then the mixture was titrated with HCl.

The saponification value was determined by:

$$\text{“Saponification value} = (B - S) * N * 56.1/w\text{”}$$

### **3.5.2.5. IODINE VALUE:**

Initially Iodine Mono chloride was prepared then it was mixed with 0.1g of biodiesel and 20mL of CCL4 then shaken and put in dark for 30min. Then, 20mL of 15% KI was added in solution then 100mL distilled water then titrated against 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O with starch as an indicator. Yellow color was vanished which indicated the end point. The procedure for blank was repeated without biodiesel.

Iodine value was calculated by:

$$\text{Iodinevalue(IV)} = (B - S) * N * 12.69/ W$$

### **3.5.2.6. CETANE NUMBER:**

Cetane number can be calculated by:

$$\text{Cetane number} = 46.3 + \frac{5458}{SV} - 0.225 * IV$$

### **3.5.2.7. CALORIFIC VALUE:**

Calorific value is the measure of energy content of fuel that can be obtained by using calorimeter using water equivalent. Calculation for Water equivalent is done by using Benzoic acid.

Initially mass of benzoic acid was calculated, for water content calculation then put in the Bomb Calorimeter and make short circuit in wire. It will lead to increase the temperature of water.

Water content was calculated by:

$(6318 * \text{wt. Of sample} + 45) / \text{rise in temp.}$

Then biodiesel was put in bomb calorimeter with oxygen filled in container and ignition was sparked.

Calorific value was calculated by:

$\text{Cv of fuel} = (\text{Water equivalent} * \text{rise in temp.} - 45) / \text{sample wt.}$

### **3.6. SUMMARY:**

This chapter illustrates the methodological framework adopted to carry out the research. Selection of catalyst and their characteristics are mentioned. Techniques and equipment which are used in characterization and measurements of flash point, viscosity, solubility test, saponification value, iodine value, cetane number of biodiesel (final product) are mentioned in detail. Detailed process of transesterification and catalyst synthesis are discussed with the help of diagrams.



# References

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## **Chapter 4:**

### **“RESULTS AND DISCUSSION”**

#### **4.1. CATALYST PREPARATION AND CHARACTERIZATION:**

After synthesis of catalyst, solid catalyst i.e. (K-CaO) is characterized by powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET) surface area measurement techniques are performed so it could be used to produce biodiesel from waste cooking oil. Results of catalytic characterization are given below.

##### **4.1.1. BET**

The surface area was calculated by BET using Quanta chrome instruments (USA). For porosity estimation, nitrogen adsorption was performed at highest relative pressure. Before analysis, degassing was carried out at 300°C to clean the surface from volatiles.

From BET result, it is found that basic strength of catalyst increased 9.8 to 11.11 with increase from in Potassium ion concentration from 0 to 3.5% wt. while further increase up to 4.5% did not create any change this is because of the alkaline nature of potassium. Potassium made a strong basic bond with CaO surface. while surface area decreased with increase in potassium ion concentration because of the blockage of pores as shown in given table.

CATALYST TYPE	BET SURFACE AREA M <sup>2</sup> /G	BASIC STRENGTH, H <sub>2</sub>
.CaO	3.963	0.9.8 < H <sub>2</sub> < 10.1.
K-CaO <sup>2.5</sup>	-----	10.1 < H <sub>2</sub> < 11.1 4
K-CaO <sup>3.5</sup>	3.8973	11.1 < H <sub>2</sub> < 15.0
K-CaO <sup>4.5</sup>	-----	-----

Table. 4.1. BET Characterization

#### 4.1.2. XRD:

The phase and structure of synthesized catalyst were observed by powder XRD using A Bruker Germany XRD analyzer equipped with Copper as X-ray source with the wavelength of 1.5406 Å catalyst was analyzed at room temperature i.e. (25°C) at an angle of diffraction (2θ) between 10 °C-70°C keeping the step size of 0.02° with time /step was 19 sec [9].

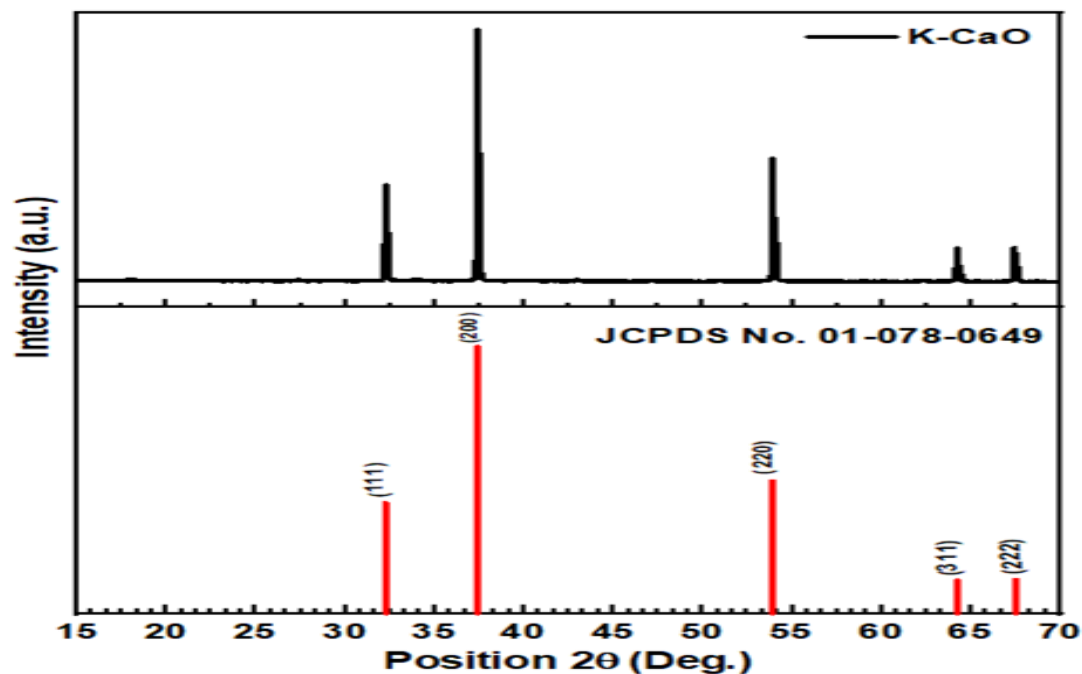


Fig.4.1. XRD curve of K-CaO-3.5

Figure 4.1 shows XRD patterns with detail crystallinity of K-CaO. The diffraction peaks were identified at  $2\theta$  37.37, 53.89, and 32.18 correspond to the d-values of 2.39, 1.69, and 2.78, respectively. The average crystallite size of 48 nm was determined using Debye-Scherrer method. K-CaO was detected at (JCPDS#. 821691)

$\text{KNO}_3$  was in very small quantity and was not detected by powder XRD may be this was the reason that diffraction pattern of  $\text{KNO}_3$  was not found.

### 4.1.3. SEM:

The morphological characteristics of catalyst were analyzed by Scanning Electron Microscopy (SEM) images by Tescan by cheque Republic; elemental analysis was also performed by using energy dispersive x-ray spectroscopy (EDS) by Oxford instruments, a built-in function of the SEM machine. 10 KV voltage was initially provided to the sample directly mounted on aluminum stubs for imaging [9]. For element analysis, beam

energy of 20KV passed through the sample for 2 minutes then the obtained raw data exported to excel for further graphing.

three different magnifications i.e. 5 $\mu$ m and 10  $\mu$ m and 20 $\mu$ m. All the results of SEM images for K-CaO show varying shapes and sizes

this study revealed synthesized K-CaO has a hexagonal, irregular shaped structure with an average size of 2-5  $\mu$ m as represented in Figure 4.2

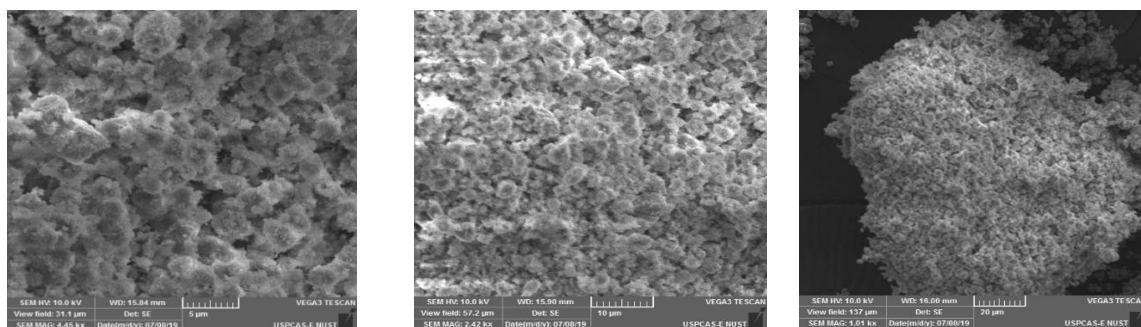


Fig.4.2. SEM images of K-CaO (a) 5 $\mu$ m, (b) 10 $\mu$ m (c) 20 $\mu$ m

#### 4.1.4. EDX:

EDX was performed for the complete compositional analysis of synthesized catalyst (K-CaO-3.5) from the given results it was identified that potassium and calcium have highest peak at 3.5 KeV in the spectrum

At normal conditions, oxygen has highest peak than calcium and potassium while carbon is also present in little quantity.

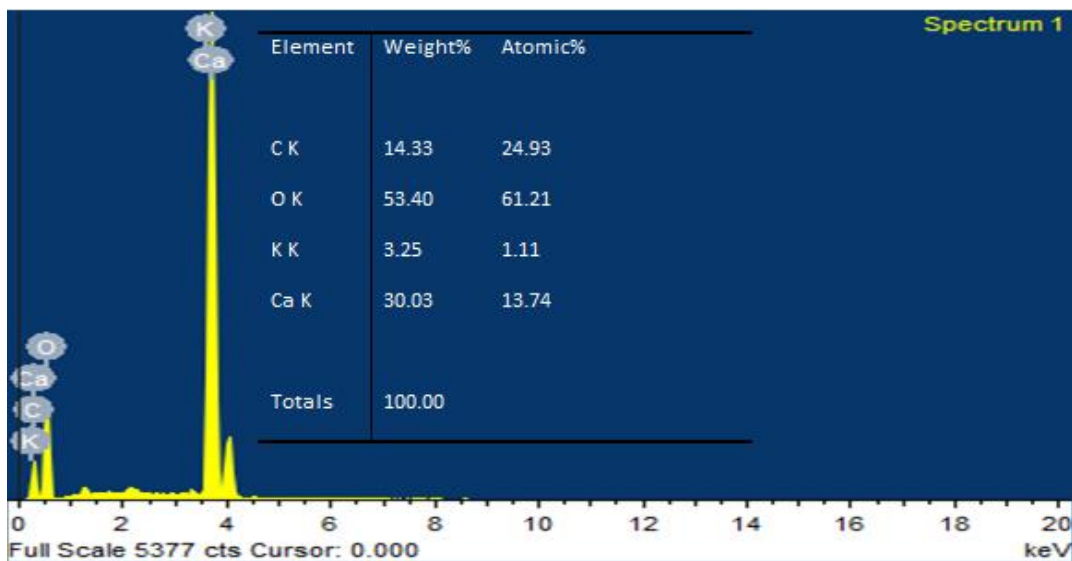


Fig.4.3. EDX pattern of K-CaO

## 4.2. TRANSESTERIFICATION REACTION AND BIODIESEL CHARACTERIZATION:

### 4.2.1. BIODIESEL YIELD:

WCO was converted into biodiesel by using catalyst K-CaO

Different parameters were considered in the reaction including:

#### 4.2.1.1. METHANOL TO OIL RATIO:

Various reactions were performed in the range of 1:12 to 18:1 with 7 wt% of K-CaO-3.5 catalyst, maximum yield of biodiesel was obtained at 12:1 methanol to oil ratio. Further increase decreased biodiesel yield because it affect the solubility of glycerin.

Methanol to Oil Ratio	Yield
9:01	62
10:01	72
11:01	82
12:01	92
13:01	90
14:01	88
15:01	86
16:01	84
17:01	82
18:01	80

Table.4.2 Methanol to Oil Ratio and Yield

#### 4.2.1.2. REACTION TIME:

Multiple reactions were performed in the range of 50 to 80 minutes with 7 wt% of K-CaO-3.5 catalyst. The reaction of 60min was found reasonable for maximum biodiesel yield further increase in reaction time caused no noteworthy change in FAME yield and increased the reaction cost.

#### 4.2.1.3. CATALYST DOSE:

Biodiesel yield was highly effected by catalyst concentration; different reactions were performed by using different catalyst concentration from 1 to 10wt%. increasing the amount of catalyst from 1 to 7% increased the biodiesel yield while further increase in catalyst dose caused soap formation which decreased biodiesel yield

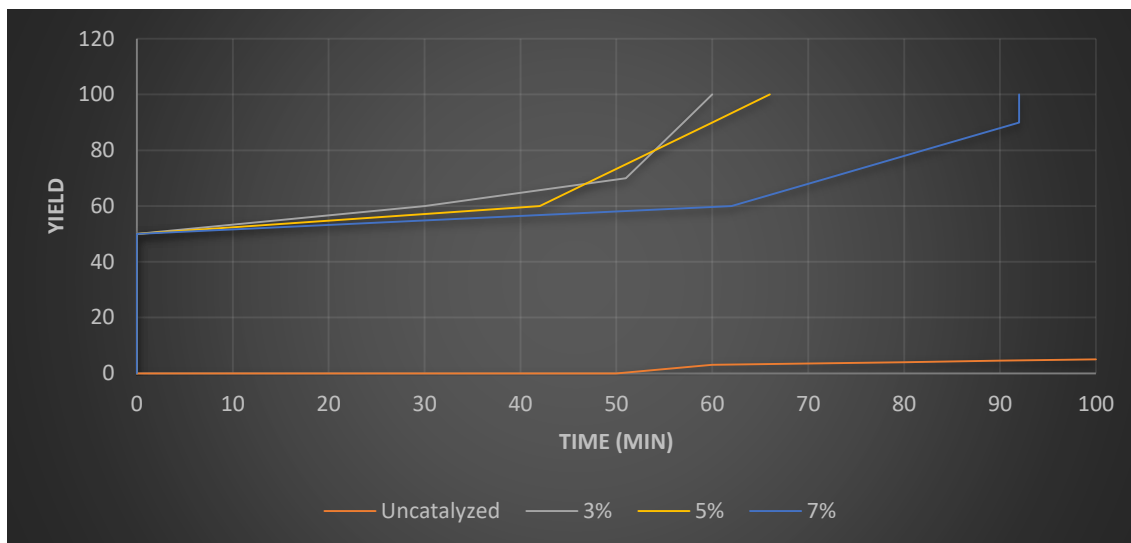


Fig.4.4. Catalyst Dose, Reaction Time and Yield

#### 4.2.1.4. POTASSIUM ION CONCENTRATION:

A variety of reactions performed by using different potassium ion concentration from 1.5 to 4.5 wt.% (K-CaO) at 60°C with 12:1 methanol to oil ratio. It was observed reaction time was decreased on increasing the potassium ion concentration from 1.5 to 3.5 wt.%. however further increase doesn't create any significance change



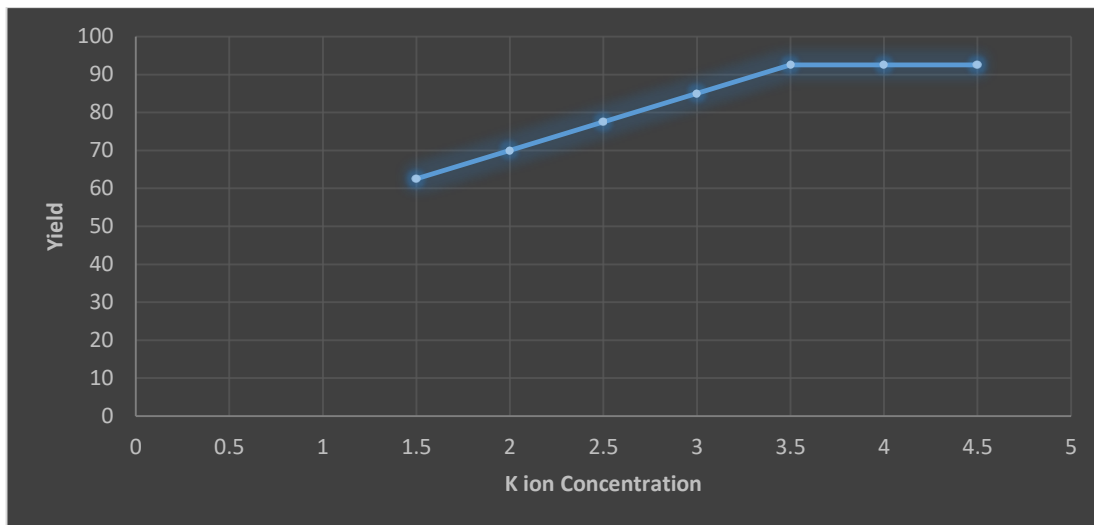


Fig.4.5. Potassium Ion Concentration and Yield

#### 4.2.1.5. TEMPERATURE:

Different reactions were performed by using different temperature ranges from 30°C to 70°C by using 7% of catalyst. FAME yield was increased till 92% as temperature was elevated from 30°C to 60°C while further elevation in temperature does not increase the FAME yield.

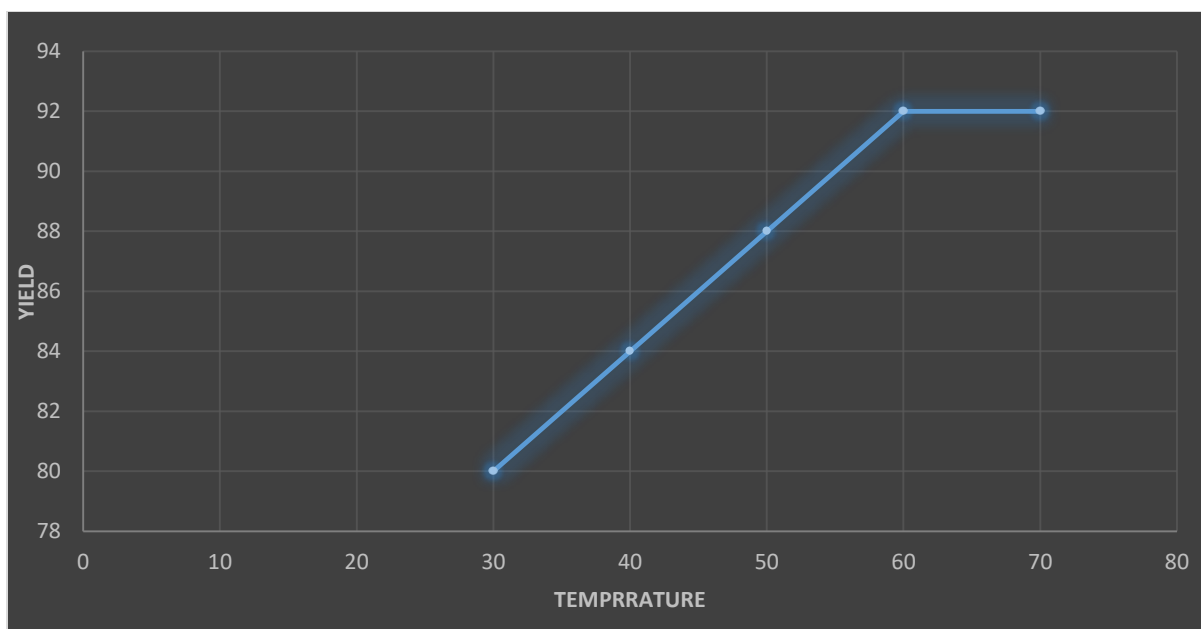


Fig.4.6. Temperature and Yield

## **4.2.2. FAME ANALYSIS:**

Properties of obtained biodiesel were analyzed by different techniques.

### **4.2.2.1. FLASH POINT:**

Biodiesel was accumulated in a vessel whilst it is ignited from the top using a source of ignition. Consequently, rise in temperature of the substance observed from origin to a point where biodiesel produced momentary flash. The temperature measured where flash occurs is termed as flash point.

### **4.2.2.2. VISCOSITY:**

Viscometer was used for the determination of viscosity, probe of viscometer was dipped in biodiesel and heated gently, at different temperatures, different readings of viscosities were noted.

### **4.2.2.3. SOLUBILITY TEST:**

solubility test of biodiesel with methanol was performed to evaluate the amount of unreacted oil in biodiesel. For this test, a mixture of biodiesel and methanol was prepared and shaken for 45 minutes with the help of magnetic stirrer and allowed to settled. After settling, biodiesel was mixed with the methanol. Although a very thin layer of unreacted oil was settled down, that indicates the purity of biodiesel.

Biodiesel yield was calculated using relation

$$\text{Yield Amountof biodiesel(\%)} = \frac{\text{Amount of biodiesel produced}}{\text{Amountof oil}} \times 100$$

#### **4.2.2.4. SAPONIFICATION VALUE**

To determine saponification value of biodiesel, ethanoic solution of KOH was prepared. 0.6 g of potassium hydroxide was dissolved in 0.5 ml of water, then ethanol was added to produce 100 ml. solution was allowed to stand in a tightly-stoppered bottle for 24 hours. 20 ml of this solution was mixed with 0.5g of biodiesel at 40°C, to make a clear solution. An indicator was put then the mixture was titrated with HCl.

The saponification value was determined by:

$$\text{“Saponification value} = (B - S) * N * 56.1/w\text{”}$$

#### **4.2.2.5. IODINE VALUE:**

Initially Iodine Mono chloride was prepared then it was mixed with 0.1g of biodiesel and 20mL of CCL4 then shaken and put in dark for 30min. Then, 20mL of 15% KI was added in solution then 100mL distilled water. then titrated against 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O using starch as an indicator. yellow color was vanished which indicated the end point. The procedure for blank was repeated without biodiesel.

Iodine value was calculated by:

$$\text{Iodinevalue(IV)} = (B - S) * N * 12.69/ W$$

#### **4.2.2.6. CETANE NUMBER:**

Cetane number can be calculated by:

$$\text{Cetane number} = 46.3 + \frac{5458}{sv} - 0.225 * IV$$

#### **4.2.2.7. CALORIFIC VALUE:**

Calorific value is the measure of energy content of fuel that can be obtained by using calorimeter using water equivalent. Calculation for Water equivalent is done by using Benzoic acid.

Initially mass of benzoic acid was calculated, for water content calculation then put in the Bomb Calorimeter and make short circuit in wire. It will lead to increase the temperature of water.

Water content was calculated by:

$(6318 * \text{wt. Of sample} + 45) / \text{rise in temp.}$

Then biodiesel was put in bomb calorimeter with oxygen filled in container and ignition was sparked.

Calorific value was calculated by:

$\text{Cv of fuel} = (\text{Water equivalent} * \text{rise in temp.} - 45) / \text{sample wt.}$

Results of physiochemical analysis are given in given table

PROPERTIES	BIODIESEL FROM WCO	BIODIESEL STANDARDS
FLASH POINT	150°C	130°C – 170°C
VISCOSITY @40°C	4.35cP	1.9 – 6.
CALORIFIC VALUE (kJ/g )	37	>35
SAPONIFICATION VALUE (mg KOH/g )	200	>312
CETANE NUMBER	51.48	≥ 47
Iodine value	63.5	<120

Table 4.3 Physiochemical Properties of Fame

### 4.3. SUMMARY:

The influence of different experiments and substrate combination ratios on Biodiesel production was investigated. Best methods and substrate combination ratios were selected. The best setup was found at 60°C with 7% catalyst dose on 12:1 methanol to oil ratio. K-CaO-3.5 was synthesized by loading 3.5 wt% of potassium in Calcium Oxide Synthesized catalyst is most effective for the biodiesel production of waste

cooking oil 92% yield of biodiesel was achieved at 12:1 methanol to oil ratio, 7% catalyst dose and 60°C reaction temperature. BET, SEM and XRD characterization were used for evaluating the quality of catalyst and compared with standards.

Biodiesel was analyzed by various physio-chemical tests and results were compared with ASTM standards. This is the most effective utilization of waste cooking oil to cater the energy crises and environmental pollution issues.

# References

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- [5] S. Mahesh, "Biodiesel Production from Waste Cooking Oil Using KBr Impregnated CaO as Catalyst," *Energy Conversion and Management Elsevier Ltd.*, vol. vol. 91, pp. 442-450, 2015.
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# Chapter 5:

## CONCLUSIONS & RECOMMENDATIONS

The following conclusion and recommendations were extracted from this study which has been compiled in the form of a thesis.

### 5.1 CONCLUSIONS

1. K-CaO-3.5 was synthesized by loading 3.5 wt% of potassium in Calcium Oxide
2. Biodiesel was successfully produced from waste cooking oil by the application of synthesized catalyst (K-CaO-3.5).
3. Free fatty acids from waste cooking oil were removed after pretreatment of waste cooking oil by the process of esterification.
4. Sulfuric acid was proved the best catalyst for efficient esterification with 88% conversion efficiency.
5. Esterified oil was reacted with methanol in the presence of synthesized catalyst under the process of transesterification to produce biodiesel
6. Synthesized catalyst (KCaO-3.5) was found most efficient for transesterification
7. By using 7% of catalyst (KCaO-3.5) reaction time was decreased to 60 minutes while temperature was reduced to 60°C
8. Maximum efficiency was obtained at 12:1 methanol to oil ratio.
9. Synthesized catalyst (KCaO-3.5 can be reused for three catalytic cycles. Although it's efficiency would be reduced
10. The quality of catalyst was evaluated through BET, SEM and XRD characterization and compared with standards.



11. Biodiesel was analyzed by various physio-chemical tests and results were compared with ASTM standards and EN 14214 specifications
12. Produced biodiesel has oleic acid, linoleic acid, palmitic acid, stearic acid as main components
13. From this study, it has been found that the KCaO-3.5 is most promising catalyst utilized for the conversion of low quality, economical waste cooking oil into valuable biodiesel.

## **5.2 RECOMMENDATIONS:**

1. Further detailed study is required for detailed catalytic study for production of biodiesel by using waste cooking oil.
2. The data obtained from this study could be used as a basic for designing large scale transesterification plant for biodiesel production from waste cooking oil.
3. K-CaO-3.5 is a very efficient catalyst and much improvement is needed for more efficient transesterification.
4. Esterification is an another field that could be study.

# Potassium Based Calcium Oxide Catalyst Synthesis for Efficient Transesterification of Waste Cooking Oil

Bushra Hassan<sup>1</sup>, Rabia Liaquat<sup>1</sup>

<sup>1</sup>*US-Pakistan Center of Advanced Study in Energy National University of Science and Technology, Islamabad,*

Biodiesel production from waste cooking oil is indeed an efficient and environment-friendly way to overcome environmental pollution and energy crisis owing to nontoxic nature of Biodiesel synthesized by Heterogeneous Catalyst (K-CaO). Utilization of waste cooking oil participates both in reducing the overall greenhouse gas emissions to minimum level and further in obtaining economical biodiesel. During synthesis, the crushed waste eggshells were calcined in muffle furnace with optimum conditions (temperature of 950 °C, retention time of 3 h). Transformed calcium species in the shells into active CaO were impregnated with Potassium i.e. K-(CaO) for transesterification. The catalyzed reaction was proven to be most efficient with molar ratio of 12:1 and temperature 64°C in the presence of 7% catalyst. The biodiesel yield from transesterification was approximately 92% of Fatty Acid Methyl Ester (FAME) produced in an hour. Furthermore, the catalytic activity in transesterification of waste cooking oil and its physicochemical properties were examined by Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) and X-Ray Diffraction (XRD). Hence the biodiesel production from waste cooking oil was proven worthy aided by catalyst K (CaO) synthesized using waste eggshells.

Keywords:

Transesterification

Waste egg shell

Biodiesel

Heterogeneous catalyst

## **INTRODUCTION:**

The diminishing traditional resources for the fuel production are responsible for increase in diesel price and diesel's toxic nature increases environmental concerns that inspire the diesel fuel replacement. Owing to this, renewable, biodegradable, nontoxic, ecofriendly and free from sulfur and aromatics nature of Biodiesel is found to be more competitive diesel for fuel substitution [1]. Production of biodiesel is feasible by utilizing number of transesterification technologies. Oils and fats (OF) are processed with alcohol (usually

methanol) and a catalyst. The reaction breaks and separates out oil molecules (triglycerides) apart and the desired yield i.e. alkyl esters (biodiesel) is obtained with glycerin as a by-product after purification and separation.

Biodiesel is produced from renewable resources like vegetable oils such as soya beans, palm, sunflower canola, jatropha, rapeseed, cottonseed and animal fats. Using edible oils and animal fats for fuel generation can shorten the food chain, furthermore animal fats have higher amount of saturated fatty acids, so it cannot be the ideal raw material [15]. Selection of the raw material creates high impact on the overall cost for producing biodiesel. Another vegetable oil i.e. Waste cooking oil (WCO) whose considerable quantity is usually dumped into landfills or rivers, which is responsible for land and water pollution. WCO is available all over the world where ever food is cooked so its usage in the biodiesel production is comparatively very economical and environmental friendly than virgin oils, [5] hence, WCO is the promising feedstock in biodiesel production.

Homogenous catalysts are fast and don't require harsh conditions in transesterification reactions but efforts are made on the production of solid (heterogeneous) catalysts because of their reusability, high purity, non-corrosive nature, longer life and easy separation of biodiesel and glycol [1] [6]. Among these catalyst alkaline earth metallic oxides like (CaO, MgO, SrO) have proven worthy because of their higher activities in the process of transesterification. Moreover, CaO is ecofriendly also. There are various feed stocks like (CaCO<sub>3</sub>, Ca(OH)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>) used for the production of Calcium oxides. [11] . Besides these, natural calcium sources like animal shells and bones can be achieved from wastes that will not only reduce catalyst cost but also helpful in waste management.

In this research, initially calcium oxide is prepared from waste eggshells, and then impregnated with the different concentrations of potassium ion to increase basicity of (CaO) alkaline catalyst used for the process of transesterification. Activity of obtained catalyst was tested with different oil to methanol ratio for producing biodiesel, followed by different techniques for analyzing obtained biodiesel properties.

## **MATERIALS AND METHODS:**

### **MATERIAL SAMPLING:**

Waste cooking oil and waste egg shells are collected from university cafeteria and hostel's mess respectively. All chemicals i.e. sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for esterification, potassium nitrate (KNO<sub>3</sub>) for catalyst impregnation, methanol (CH<sub>3</sub>OH) for transesterification were available in university's laboratory

### **CATALYST SYNTHESIS:**

Waste egg shells were collected from hostel mess and cleaned from contaminants using distilled water, then dried at 90°C for 4 hours. The dried egg shells were crushed and

grinded in grinder to form  $\text{CaCO}_3$  powder. The obtained powder then fed to calcination section for 2 hours at  $900^\circ\text{C}$  to form Calcium oxide (CaO) [11]. Calcium oxide converted in K-CaO using wet impregnation method. Distilled water (40ml) was used to dissolve 10g of CaO to make a solution initially with 10 ml potassium nitrate aqueous solution with different concentrations was also added to gain potassium ion doped calcium oxide. The obtained mixture was stirred at 500 RPM for 3 hours at ambient temperature followed by drying  $180^\circ\text{C}$  for 24 hours and finally calcined for an hour at  $750^\circ\text{C}$ . The obtained catalyst was termed as K-CaO-XX where XX represents potassium concentration (i.e. 2-4%) [2]

### **PRETREATMENT OF WCO:**

Initially waste cooking oil (WCO) was collected locally from university's canteen then its pretreatment was performed by preheating and filtration to remove solid food particles. After that, esterification is performed with acid catalyst i.e. sulfuric acid to remove free fatty acids. [9] In esterification, 25ml of methanol and 2ml of sulfuric acid were mixed with 100ml of waste cooking oil. Afterwards, the mixture poured in a conical flask of 250ml capacity for invariable stirring of the mixture using a magnetic stirrer for an hour. The conical flask was then placed on hot plate at  $55^\circ\text{C}$ . After stirring mixture was filtered to separate solid catalyst, then settled for 24 hours, so excess fatty acids can easily be removed. Now the oil is ready for transesterification [2]

### **TRANSESTERIFICATION OF PRETREATED WCO**

In this process methanol is processed with waste cooking oil in presence of a catalyst. Mixture of waste cooking oil, methanol and catalyst (K-CaO) preheated at  $60^\circ\text{C}$  and then added to pretreated oil. Afterwards, the mixture poured in a conical flask for constant stirring of the mixture using a magnetic stirrer for 60 mins. Transesterification was carried with different oil to methanol ratio (9:1 to 15:1) and catalyst concentration(1-4% wt). After the continuous stirring for an hour, components of waste cooking oil disintegrated into products. The triglycerides were transformed into methyl esters (biodiesel), then catalyst removed by filtration, methanol by evaporation and glycol is separated by gravity settling. After washing excess methanol was removed and desired biodiesel was obtained. [4]

### **CHARACTERIZATION:**

#### **SYNTHESIZED CATALYST CHARACTERIZATION:**

For further enhancement in research, solid catalyst i.e. (K-CaO) is characterized by powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET) surface area measurement techniques are performed so it can be applied in transesterification of WCO.

### **X-RAY DIFFRACTION (XRD):**

The phase and crystalline structure of synthesized catalyst were studied by powder X-ray diffraction (XRD) using A Bruker Germany XRD analyzer equipped with Cu as X-ray source with the wavelength of 1.5406 Å. Catalyst was analyzed at room temperature i.e. (25°C) at an angle of diffraction ( $2\theta$ ) between 10°C-70°C keeping the step size of 0.02° with time /step was 19 sec. [14]

### **SCANNING ELECTRON MICROSCOPY (SEM):**

The morphological characteristics of catalyst were analyzed by Scanning Electron Microscopy (SEM) images by Tescan by cheque Republic; elemental analysis was also performed by using energy dispersive x-ray spectroscopy (EDX) by Oxford instruments, a built-in function of the SEM machine. 10 KV voltage was initially provided to the sample directly mounted on aluminum stubs for imaging. [14]. For element analysis, beam energy of 20KV passed through the sample for 2 minutes then the obtained raw data exported to excel for further graphing.

### **BRUNAUER EMMETT TELLER (BET):**

The principle of Brunauer Emmett Teller (BET) was used to calculate the surface area by Quanta chrome instruments (USA). For porosity estimation, nitrogen adsorption was performed at highest relative pressure. Before analysis, degassing was carried out at 300°C to clean the surface from volatiles.

### **FAME CHARACTERIZATION:**

Properties of obtained biodiesel were analyzed by different techniques.

### **FLASH POINT:**

Biodiesel was accumulated in a vessel whilst it is ignited from the top using a source of ignition. Consequently, rise in temperature of the substance observed from origin to a point where biodiesel produced momentary flash. The temperature measured where flash occurs is termed as flash point.

### **VISCOSITY:**

Viscometer was used for the determination of viscosity, probe of viscometer was dipped in biodiesel and heated gently, at different temperatures, different readings of viscosities were noted.

### **SOLUBILITY TEST:**

solubility test of biodiesel with methanol was performed to evaluate the amount of unreacted oil in biodiesel. For this test, a mixture of biodiesel and methanol was prepared and shaken for 45 minutes with the help of magnetic stirrer and allowed to settle. After settling, biodiesel was mixed with the methanol. Although a very thin layer of unreacted oil was settled down, that indicates the purity of biodiesel biodiesel yield was calculated using relation

$$\text{Yield Amount of biodiesel(\%)} = \frac{\text{Amount of biodiesel produced}}{\text{Amount of oil}} \times 100$$

### **SAPONIFICATION VALUE**

To determine saponification value of biodiesel, ethanolic solution of KOH was prepared. 0.6 g of potassium hydroxide was dissolved in 0.5 ml of water, then ethanol was added to produce 100 ml. solution was allowed to stand in a tightly-stoppered bottle for 24 hours. 20 ml of this solution was mixed with 0.5g of biodiesel at 40°C, to make a clear solution. An indicator (Phenolphthalein) was added then the mixture was titrated with HCl

The saponification value was determined by:

$$\text{Saponification value} = (B - S) * N * 56.1/w$$

### **IODINE VALUE:**

Initially Iodine Mono chloride was prepared then it was mixed with 0.1g of biodiesel and 20 ml. of CCl<sub>4</sub> then shaken and put in dark for 30min. Then, 20 ml. of 15% KI was added in solution then 100 ml. distilled water. then titrated against 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O using starch as an indicator. Yellow color was disappeared which indicated the end point. Entire procedure was repeated for blank without biodiesel.

iodine value was calculated by:

$$\text{Iodine value(IV)} = [(B - S) * N * 12.69] / W$$

### **CETANE NUMBER:**

Cetane number can be calculated by:

$$\text{Cetane number} = 46.3 + \frac{5458}{SV} - 0.225 * IV$$

### **CALORIFIC VALUE:**

Calorific value is the measure of energy content of fuel. that can be obtained by using calorimeter by using water equivalent. Water equivalent is calculated by using Benzoic acid.

Initially mass of benzoic acid was calculated, for water content calculation then put in the Bomb Calorimeter and make short circuit in wire. It will lead to increase the temperature of water.

Water content was calculated by:

$$(6318 * \text{wt. Of sample} + 45) / \text{rise in temp.}$$

Then biodiesel was put in bomb calorimeter with oxygen filled in container and ignition was sparked.

Calorific value was calculated by:

$$Cv \text{ of fuel} = (\text{Water equivalent} * \text{rise in temp.} - 45) / \text{sample wt.}$$

## RESULTS AND DISCUSSIONS:

### CATALYST PREPARATION AND CHARACTERIZATION:

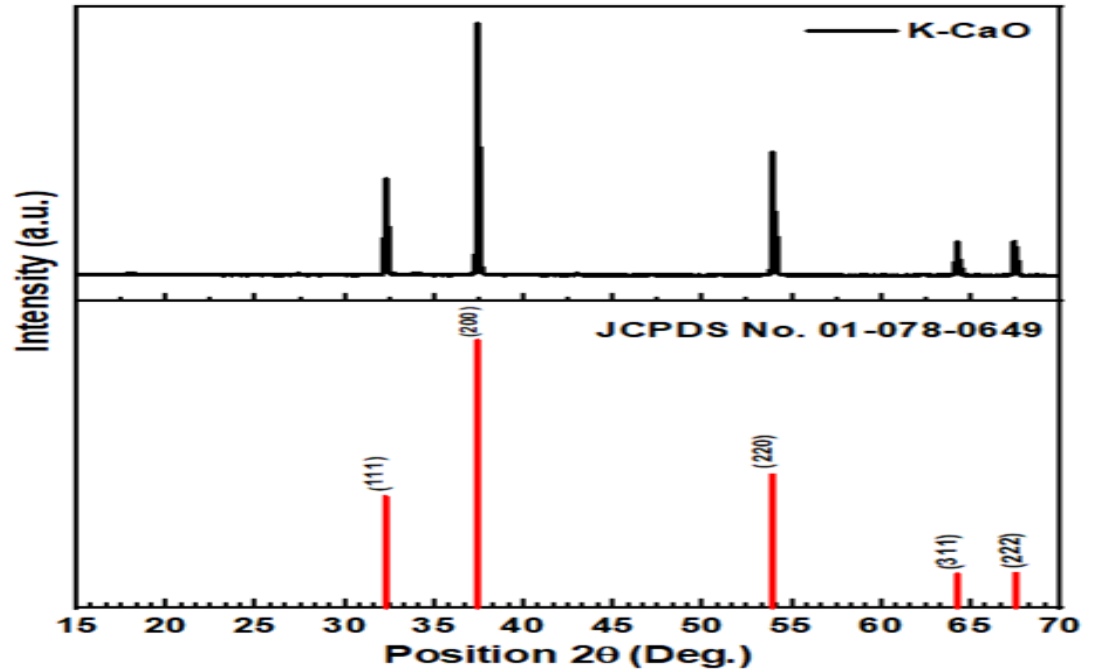
#### 1. BRUNAUER EMMETT TELLER (BET)

From BET result, it is found that the basic strength of catalyst increased with increase in Potassium ion concentration because of the alkaline nature of potassium while surface area decreased with increase in potassium ion concentration because of the blockage of pores as shown in given table.

CATALYST TYPE	BET SURFACE AREA M <sub>2</sub> /G	BASIC STRENGTH, H <sub>+</sub>
CaO	3.963	9.8 < H <sub>+</sub> < 10.1
K-CaO2.5	-----	10.1 < H <sub>+</sub> < 11.1 4
K-CaO3.5	3.8973	11.1 < H <sub>+</sub> < 15.0
K-CaO4.5	-----	-----

#### 2. X-RAY DIFFRACTION (XRD):

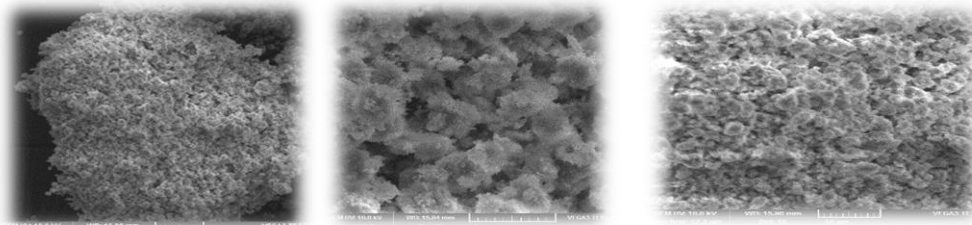
The results of powder XRD of K- CaO-3.5 shows in figure, the peak was found at t 2θ = 37:37



. XRD curve of K-CaO-3.5

### 3. SCANNING ELECTRON MICROSCOPY (SEM):

From SEM results of K-CaO-3.5, morphology of irregular and hexagonal shaped clusters was found size 2–5 μm- particles as shown in given Figure



(a) 5μm,

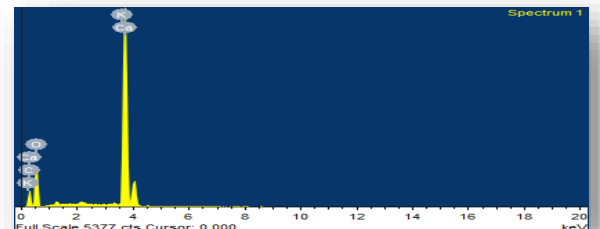
(b) 10μm

(c) 20μm

SEM images of K-CaO

EDX was used for the elemental analysis or chemical characterization of K-CaO=3.5. results are shown below

Element	Weight%	Atomic%	
C K	9.87	17.15	
O K	42.56	56.25	
K K	2.80	1.67	
Ca K	44.77	23.62	
Totals	100.00		





EDX pattern of K-CaO

## **TRANSESTERIFICATION REACTION AND BIODIESEL CHARACTERIZATION:**

### **BIODIESEL YIELD:**

WCO was converted into biodiesel by using catalyst K-CaO. Different parameters were considered in the reaction including:

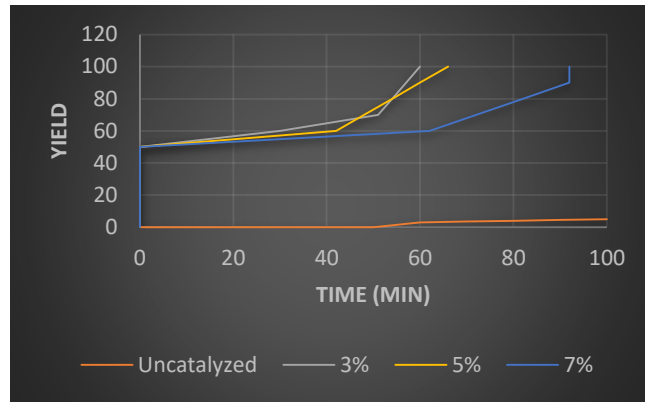
#### **METHANOL TO OIL RATIO:**

Various reactions were performed in the range of 1:12 to 18:1 with 7 wt% of K-CaO-3.5 catalyst, maximum yield of biodiesel was obtained at 12:1 methanol to oil ratio. Further increase decreased biodiesel yield because it affect the solubility of glycerin.

METHANOL TO OIL RATIO	YIELD
9:01	62
10:01	72
11:01	82
12:01	92
13:01	90
14:01	88
15:01	86
16:01	84
17:01	82
18:01	80

#### **CATALYST DOSE:**

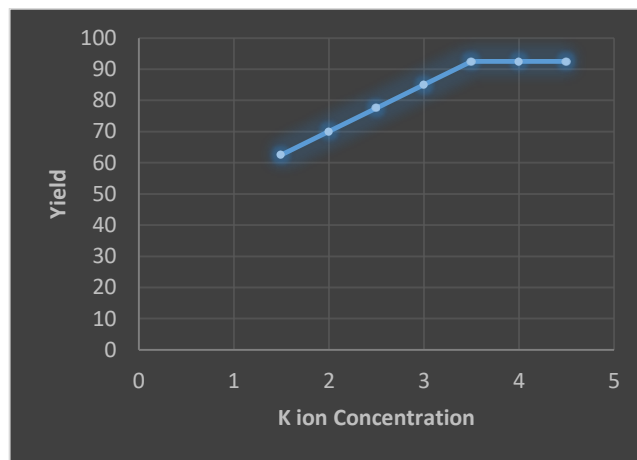
Biodiesel yield was highly effected by catalyst concentration; different reactions were performed by using different catalyst concentration from 1 to 10wt%. increasing the amount of catalyst from 1 to 7% increased the biodiesel yield while further increase in catalyst dose caused soap formation which decreased biodiesel yield



Catalyst Dose, Reaction Time and Yield

### POTASSIUM ION CONCENTRATION:

A variety of reactions performed by using different potassium ion concentration from 1.5 to 4.5 wt.% (K-CaO) at 60°C with 12:1 methanol to oil ratio. It was observed reaction time was decreased on increasing the potassium ion concentration from 1.5 to 3.5 wt.%, however further increase doesn't create any significance change



Potassium Ion Concentration and Yield

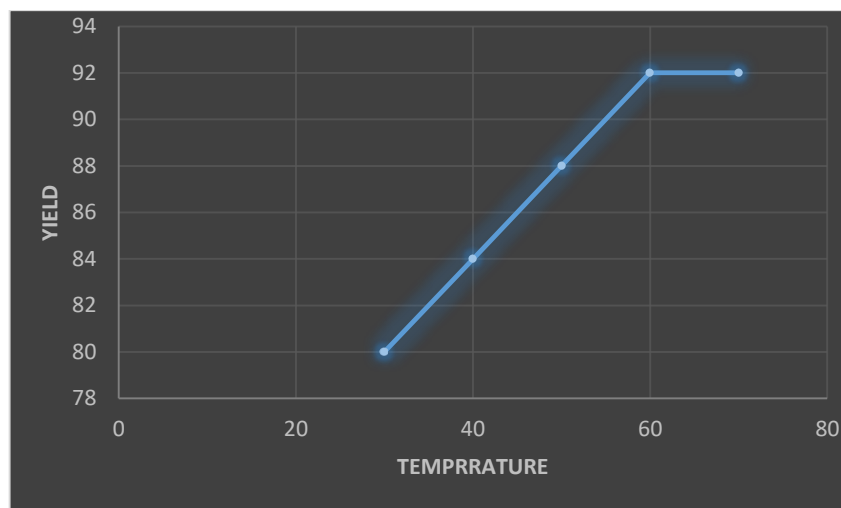
### REACTION TIME:

Various reactions were performed in the range of 50 to 80 minutes with 7 wt% of K-CaO-3.5 catalyst. The reaction of 60min was found suitable for maximum biodiesel yield further increase in reaction time caused no significant change in FAME yield

### TEMPERATURE:

Different reactions were performed by using different temperature ranges from 30°C to 70°C by using 7% of catalyst. FAME yield was increased from 80.4% to 94% as

temperature was increased from 30°C to 60°C while further increase in temperature does not increase the FAME yield.



Temperature and Yield

**PHYSIO-CHEMICAL PROPERTIES OF BIODIESEL:**

PROPERTIES	BIODIESEL FROM WCO	BIODIESEL STANDARDS
FLASH POINT	150°C	130°C – 170°C
VISCOSITY @40°C	4.35cP	1.9 – 6
CALORIFIC VALUE (kJ/g )	37	>35
SAPONIFICATION VALUE (mg KOH/g )	200	>312
CETANE NUMBER	51.48	≥ 47
Iodine value	63.5	<120

**CONCLUSION:**

1. K-CaO-3.5 was synthesized by loading 3.5 wt% of potassium in Calcium Oxide
2. Synthesized catalyst is most effective for the biodiesel production of waste cooking oil
3. Flash point was found at 150°C
4. 92% yield of biodiesel was obtained at 12:1 methanol to oil ratio, 7% catalyst dose and 60°C reaction temperature

5. The quality of catalyst was evaluated through BET, SEM and XRD characterization and compared with standards.
6. Biodiesel was analyzed by various physio-chemical tests and results were compared with ASTM standards
7. This is the best utilization of waste cooking oil to decrease the energy crises and environmental pollution issues.

## **REFERENCES:**

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