

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

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Abstract: 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

I. 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 (Balat). 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 (Mahesh et al.). 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, (Canakci and Van Gerpen) 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 (Balat) (Demirbas). 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 (CaCO₃, Ca(OH)₂, Ca(NO₃)₂) used for the production of Calcium oxides. (Cho et al.). 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.

II. MATERIALS AND METHODS:

2.1 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 (H₂SO₄) for esterification, potassium nitrate (KNO₃) for catalyst impregnation, methanol (CH₃OH) for transesterification were available in university's laboratory

2.2 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 CaCO₃ powder. The obtained powder then fed to calcination section for 2 hours at 900°C to form Calcium oxide (CaO) (Viriya-Empikul et al.). 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-XX where XX represents potassium concentration (i.e. 2-4%)(Kumar and Ali)

2.3 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.(Chai et al.)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(Sahar et al.)

2.4 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.(Sahar et al.)

III. CHARACTERIZATION:

3.1 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.

3.1.1 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 (2θ) between 10°C-70°C keeping the step size of 0.02° with time /step was 19 sec.(Jairam et al.)

3.1.2 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.(Jairam et al.). 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.

3.1.3 Brunauer Emmett Teller (Bet):

The principle of Brunauer Emmett Teller (BET) was used to calculate the surface area by Quantachrome 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.

3.2 Fame Characterization:

Properties of obtained biodiesel were analyzed by different techniques.

3.2.1 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.

3.2.2 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.

3.2.3 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 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

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

3.2.4 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 (Phenolphthalein) was added then the mixture was titrated with HCL

The saponification value was determined by:

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

3.2.5 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 Na2S2O3.5H2O 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:

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

3.2.6 Cetane Number:

Cetane number can be calculated by:

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

3.2.7 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:

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

IV. RESULTS AND DISCUSSIONS:

4.1 Catalyst Preparation and Characterization:

4.1.1 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 1.

CATALYST TYPE	BET SURFACE AREA M ² /G	BASIC STRENGTH, H ₊
CaO	3.963	9.8 < H ₊ < 10.1
K-CaO _{2.5}	-----	10.1 < H ₊ < 11.14
K-CaO _{3.5}	3.8973	11.1 < H ₊ < 15.0
K-CaO _{4.5}	-----	-----

4.1.2 X-Ray Diffraction (XRD):

The results of powder XRD of K- CaO-3.5 shows in figure 1, the peak was found at $2\theta = 37:37$

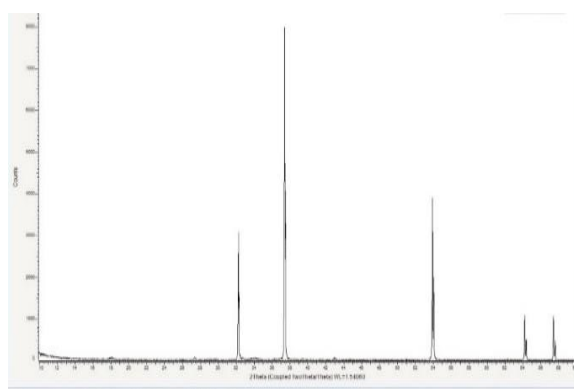


Fig. 1

4.1.3 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 2.

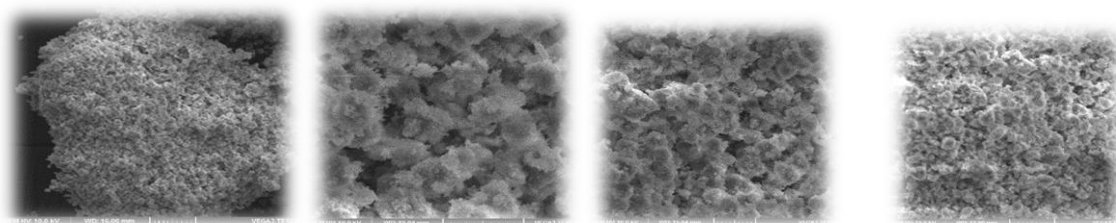


Fig. 2

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	

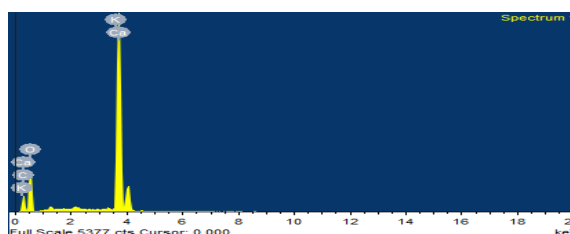


Fig. 3

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.

Table. 2

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

4.2.1.2 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

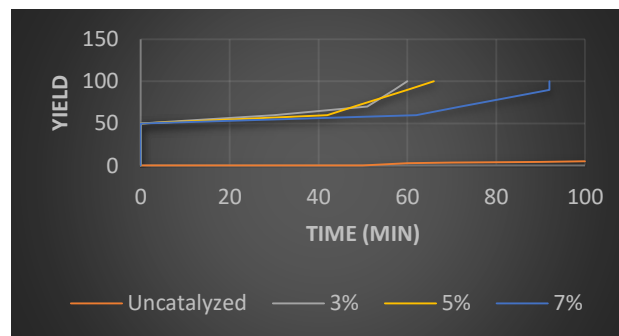


Fig. 4

4.2.1.2.1 Potassium Ion Concentration:

A variety of reactions performed by using different potassium ion concentration from 1.5 to 4.5 wt.% (K-CaO) at 60C 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

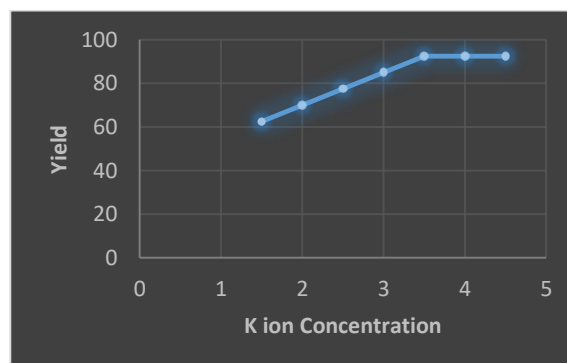


Fig. 5

4.2.1.3 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

4.2.1.4 Temperature:

Different reactions were performed by using different temperature ranges from 30C to 70C 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.

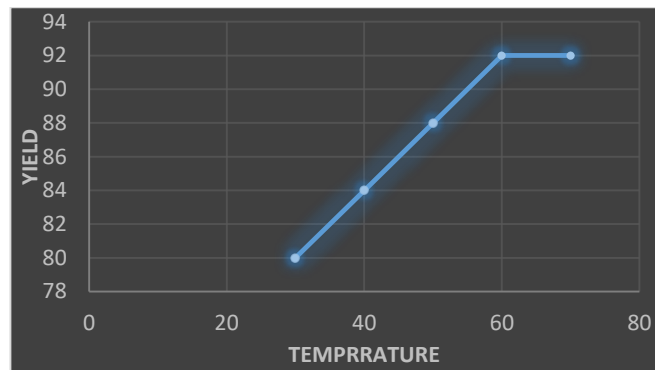


Fig. 6

4.2.2 Physico-Chemical Properties Of Biodiesel:

Table. 2

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

V. 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. 92% yield of biodiesel was obtained at 12:1 methanol to oil ratio, 7% catalyst dose and 60°C reaction temperature
4. The quality of catalyst was evaluated through BET, SEM and XRD characterization and compared with standards.
5. biodiesel was analyzed by various physico-chemical tests and results were compared with ASTM standards
6. This is the best utilization of waste cooking oil to decrease the energy crises and environmental pollution issues.

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