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Application of Solid Base Calcium Oxide as a Heterogeneous Catalyst for the Production of Biodiesel

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Abstract: Biodiesel is the monoalkyl esters of long chain fatty acids, derived from vegetable oils and animal fats. The biodiesel was produced from waste frying oil with methanol using Calcium Oxide catalyst by transesterification. The waste chicken egg shell was utilized as a bio resource of calcium oxide (CaO) in catalyzing a transesterification to produce biodiesel (methyl ester). The economic and environment-friendly catalysts were prepared by a calcination method. The experimental results was found that the maximum yield of fatty acid methyl ester was 92% at the following reaction conditions: reaction temperature of 60°C, a reaction period of 4 h, a ratio of methanol to oil at 9:1, and amount of catalyst at 9% wt of oil. The heterogeneous base catalyst CaO can be successfully utilized for the production of Biodiesel.
Key Words: Biodiesel, Heterogeneous and Transesterification.

1. Introduction

In recent years, biodiesel has gained international attention as a source of alternative fuel due to its quality like high degradability, no toxicity, and low emission of carbon monoxide, particulate matter and unburned hydrocarbons (1, 2). Because of recent energy crisis, H_2 energy (3), solar energy (4), and biodiesel (5, 6), have been strong-minded worldwide. Diesel consumption in India as in 2005 has increased significantly in 2013-14. This shows that the fossil fuels are depleting at a higher rate thus demanding an alternate renewable source of energy. Biodiesel is the most potential alternative energy source because it is renewable and environmental friendly. Biodiesel is the monoalkyl esters of long chain fatty acids, and produced by transesterification of vegetable oils or animal fats with methanol and can be catalyzed by an acid, base, enzymes to produce fatty acid methyl ester (FAME) and glycerol as a by-product (7,8).

The Biodiesel production proceeds by conventional process in transesterification using homogeneous catalytic process have some drawbacks like production of wastewater from washing process of catalyst residues and catalyst unreusability (9). In Heterogeneous catalysts the process of separation, regeneration and numbers of reuse is easy and cheap (10). Heterogeneous basic catalysts include alkaline earth metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and hydrotalcites (11, 12). CaO is closely resembled to an environmental-friendly material. Generally, $CaCO_3$, $Ca(NO_3)_2$ or $Ca(OH)_2$ is the basic raw material to produce CaO. Calcium carbonate, the major constituent of the eggshell (96%), is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystal) (13). Using eggshell wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the heterogeneous catalysts with high cost effectiveness.

In addition to that, wastes there are several natural calcium sources such as eggshell, mollusk shell, and bone. Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the catalysts with high cost effectiveness. (14, 15) examined that eggshells and mud crab shell could

be used as a catalyst for biodiesel production. (16) Found that transesterification of soybean oil Catalyzed by combusted oyster shell and it is active for biodiesel production. All these works exposed that the waste shell-derived catalyst showed high potential to be used as a low-cost biodiesel production catalyst. Recently, the function of normal calcium sources from waste materials has been considered as a new trend for biodiesel production (17). In this work, we have carried out transesterification using the chicken eggshell wastes as economical and environment-friendly catalyst. Biodiesel conversion was measured by HPLC. The objective was to optimize the process for biodiesel production from waste frying oil using CaO catalyst. The effects of reaction time, reaction temperature, methanol to oil molar ratio, and amount of catalyst of catalyst were investigated.

2. Experimental

2.1. Materials

Waste Frying Oil was purchased from Restaurants in Chidambaram, Cuddalore District, and Tamil Nadu. The density of the oil was measured to be 0.864g/cm^3. The chicken eggshell was collected as wastes from Restaurants in Chidambaram, Cuddalore District, and Tamil Nadu. The eggshell was rinsed with running water to remove dust and impurities, and then dried in an oven. All chemicals were analytical-grade reagents (Merck, >99% purity) and were used as received.

The physical properties, like the specific gravity, kinematic viscosity, free fatty acid content, moisture content, saponification value, odour, colour was measured by the methods was mentioned above and presented in Table 1

Table 1. Raw material (Waste frying oil) specification

Property name	Value
Specific gravity, at 25°C	0.92
Kinematic viscosity (mm^2/s), at 40°C	52.0
Free fatty acid content (%)	4.5
Moisture content (%)	0.08
Saponification value (mg KOH/gm oil)	194
Odour	Mild flavour
Colour	Light Brown

2.2. Preparation of Eggshell Waste-Derived Catalyst

CaO catalyst was prepared from waste eggshell by calcination method. The waste eggshell was cleaned thoroughly with running water for removal of organic matter and dried for whole night at 102°C, and then the waste eggshell (100-200 mesh) was calcined at 900°C in air atmosphere with a heating rate of 10°C/min for 4h (17). The product was obtained as white powder. All calcined samples were kept in the close vessel to avoid the reaction with humidity in air and carbon dioxide (CO_2) before used. Because the CaO catalyst will be poisoned by CO_2 and convert into $CaCO_3$, thus reducing its activity as a catalyst. Catalyst separation, catalyst reusability, production purification, less energy and water consumption is the special advantages of using heterogeneous catalyst (18). Among the alkaline earth metal oxides, calcium oxide (CaO) is the promising heterogeneous catalyst for biodiesel production (19).

2.3. Analysis of biodiesel by HPLC

A general benefit of HPLC compared to GC is that time, and reagent consuming derivatizations are not necessary, which reduces analyses times. However, there are fewer reports of HPLC applied to biodiesel than GC analysis (20). Biodiesel was analyzed using high performance liquid chromatography (HPLC) from Shimadzu, Japan equipped with refractive index detector (RID). Silica-gel column (c18) was used to determine the FAME yield. 100 µL of the rinsed product was diluted in 3 mL of hexane and was injected into HPLC column. The column temperature was maintained at 40 °C and the mobile phase was n-hexane/2-propanol = 99.5/0.5 (v/v). Methyl oleate was used as standard to determine FAME. The yield was calculated using equation (1) which has been reported by (21)

Yield = (CFAME / 3Coil) x 100 **.....** (1)

Where CFAME is the molar concentration of FAME in the product and Coil is the molar concentration of triglycerides in the feedstock, respectively as described in equation (2) and (3);

CFAME = (ρME / MWME) x Area of FAME ...(2)
Coil = (ρoil / MWoil) x Area of methyl oleate .. (3)

Where,

ρME - Density of methyl oleate,
ρoil - Density of waste frying oil,
MWME - Molecular weight of methyl oleate,
MWoil - Molecular weight of waste frying oil.

2.4. Transesterification Process

Transesterification reactions were performed in a 250ml 3-necked round bottom flask. One of side neck was fitted with a water-cooled condenser, the middle neck was used to insert magnetic stirrer and other raw materials in it, and the third neck was fitted with a temperature indicating thermometer. The speed of the magnetic stirrer was monitored. The transesterification process parameters such as amount of catalyst, methanol to oil ratio, reaction temperature and reaction time were varied to attain maximum methyl ester conversion. By inserting methanol into a flask with a variable ratio of 7:1, 9:1, 11:1 mol ratio of methanol to oil. Secondly, adding CaO catalyst as many as 8% of the mass of the oil. After a homogeneous mixture, Waste Frying oil is inserted into a flask and heated at a variable temperature 55,60,65^{o}C in 3,4,5 hours of stirring. After the reaction is completed, the catalyst was screened by using a filter paper (0.7 μm) and the transesterification products were allowed to settle overnight for the clear separation of biodiesel and glycerol. The upper layer fatty acid methyl esters, formed by the conversion of fatty acids to their respective esters are termed as biodiesel and the lower dense layer is termed as glycerol.

2.5. Analysis for oil and biodiesel

Analysis of Free Fatty Acid content in the oil was analysed by using titrimetric methods, To determine free fatty acid of sample, 10 g of sample were dispersed in 50ml of 95% alcohol, neutralized with dil.NaOH, heated in water bath followed by titration against 0.1N NaOH until a faint pink colour persist. Saponification value (SV) was determined by the method described by (22) 5g of sample was taken with 50 ml alcoholic KOH, heated for one hour in a steam bath with occasional shaking and titrated the excess KOH with the 0.5 N hydrochloric acid till the pink colour disappeared. Physical properties such as colour, moisture content and density of the oil were determined. Properties of the produced biodiesel and comparison with biodiesel standard are given in Table 2.

Table 2. Properties of biodiesel produced from waste frying oil and comparison with standard value

Properties	Produced biodiesel value	Biodiesel Standard (25,26)	Diesel standard (26)
Specific gravity, at 25 ^{o}C	0.83	0.88 (at 15.50 C)	0.85(at 15.50 C)
Kinematic viscosity (mm2/s), at 40^{o}C	5.3	1.9–6.0	1.3 – 4.1
Free fatty acid content(%FFA)	0.5	-	-
Calorific value (Mj/Kg)	38.0	37.5	42
Moisture content (%)	0.12	0.05%	Max 0.161
Flash point (^{o}C)	135	100 to 170	60 to 80
Iodine value	88	-	-
Saponification value	194	-	-

3. Results and Discussion

Production of Biodiesel by heterogeneous catalyst transesterification of waste frying oil with methanol is relatively slow and needs high temperature to achieve a higher conversion. All the reactions were carried out at refluxing temperature. The effects of reaction parameters were explored as follows.

3.1 Effect of methanol to oil molar ratio

The methanol to oil molar ratio is one of the most important variables affecting the conversion of waste frying oil to biodiesel. The transesterification of waste frying oil required three molars of methanol for each mole of oil. Since the reaction was a reversible reaction, biodiesel conversion increased with increasing of the molar ratio of methanol to oil over the range from 3:1 to 11:1 and the results are illustrated in Figure 1. The highest conversion (95%) was obtained at the molar ratio of 9:1 for 4 h. However, further increases in the methanol to oil molar ratio, did not promote the reaction, it is understood that the glycerol would largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the reactants and catalyst thus interfering with the separation of glycerine, which in turn lowers the conversion by shifting the equilibrium in the reverse direction. Therefore, the optimal molar ratio of methanol and waste frying oil was to be 9:1.

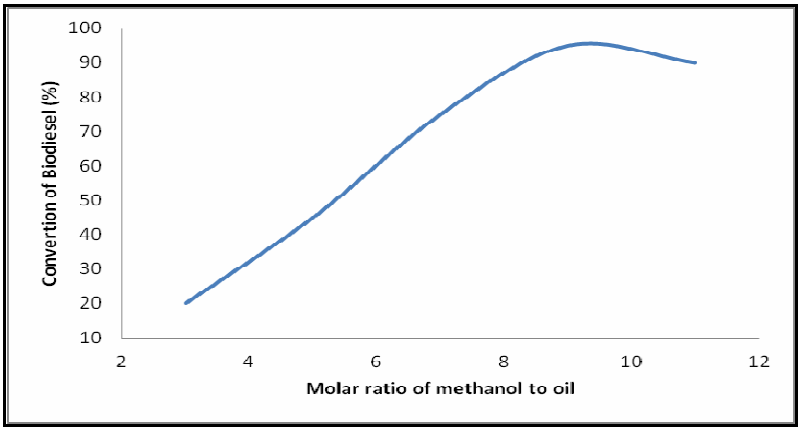

Figure 1. Conversion of waste frying oil to biodiesel at different methanol to oil molar ratio (Reaction temp. 60°C, Catalyst concentration 9% wt of oil, Reaction time 4.0 hr, under vigorous stirring)

3.2 Effect of catalyst concentration on transesterification

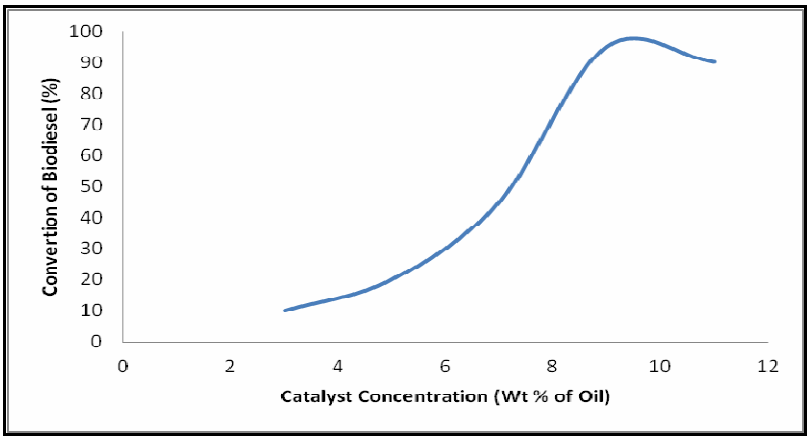

Figure 2. Conversion of waste frying oil to biodiesel at different catalyst concentration (Reaction temp. 60°C, methanol to oil ratio 9:1, Reaction time 4 h, with vigorous stirring)

The conversion of biodiesel from waste frying is severely affected by catalyst concentration. The effect of catalyst concentration on the conversion of biodiesel was investigated within the range of 3.0-11.0% CaO (based on the oil weight) and the results are illustrated in Figure 2. With increasing of the amount of catalyst from 5.0% to 9.0%, the conversion of biodiesel increased rapidly, which could be attributed to the availability of more basic sites. Further increase in catalyst concentration does not increase the conversion; it is indicating

that the catalyst amount was enough for the transesterification of waste frying oil. Too much catalyst could only make the mixture of reactants too viscous, leading to the problem of mixing and separation. In order to avoid this problem and reduce the costs, the optimum amount of the catalyst was to be 9.0% CaO (on the basis of oil weight).

3.3 Effect of temperature on transesterification

Temperature is another important variable that affecting the conversion of biodiesel. An increase in reaction temperature led to increase the biodiesel yields. Usually higher temperature is required for heterogeneous catalysed transesterification reaction. The reaction was conducted from 45-65^{o}C temperature and the results are illustrated in Figure 3. When the reaction temperature was less than 45^{o}C the conversion was less than 30%. With increasing the temperature from 45^{o}C to 60^{o}C the conversion of biodiesel increased rapidly. When the temperature was above 60^{o}C which is above the boiling point of methanol, the solvent vaporised and remained in the vapour phase in the reactor causing a reduction in the methanol in the reaction media. It is indicating that the temperature of 60^{o} C was enough for the transesterification of waste frying oil. The optimum temperature was to be 60^{o} C

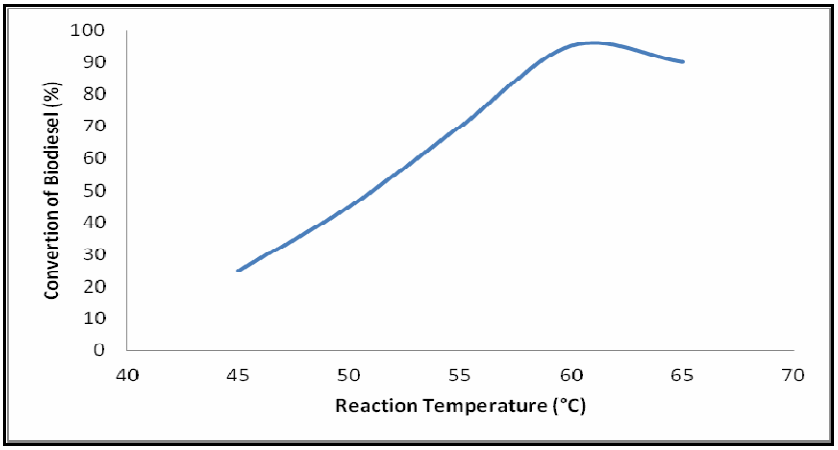

Figure 3. Conversion of waste frying oil to biodiesel at different temperature (methanol to oil ratio 9:1, catalyst concentration 9.0% CaO, Reaction time 4h, under reflux with Vigorous stirring)

3.4 Effect of reaction time on the conversion of oil to biodiesel

The effect of reaction time on the conversion of biodiesel at the catalysis of CaO was studied and the results are shown in Figure 4. The reaction time was varied within the range from 0 to 5h. The reaction time for the transesterification increases with increases the conversion rate of biodiesel was observed with the increasing of time up to 4h, and there was no further increase in the yield. Therefore the optimum reaction time was 4h, at which the highest biodiesel conversion obtained.

Figure 4. Conversion of waste frying oil to biodiesel at different reaction time (methanol to oil ratio 9:1, reaction temperature 60^{o}C, catalyst concentration 9.0% CaO, under reflux with vigorous stirring)

4. Conclusion

The eggshell wastes are used as the catalyst for the production of biodiesel process. This eggshell waste contains $CaCO_3$ which is converted to CaO after calcination at temperatures 900°C for 4h and CaO was acknowledged as an effective heterogeneous catalyst for the transesterification of waste frying oil and methanol. The effect of reaction conditions, which yield a conversion of 92% biodiesel, were reaction time 4h, reaction temperature 60°C, methanol to oil molar ratio 9:1, and catalyst concentration 9% wt of oil. The experimental results show that CaO catalyst had excellent activity and stability during transesterification reaction. As a heterogeneous catalyst, CaO can reduce the cost of biodiesel production. It has potential for industrial application in the transesterification of waste frying oil to FAME.

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