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OPTIMIZATION AND PRODUCTION OF BIODIESEL USING CALCIUM OXIDE AS A HETEROGENEOUS CATALYST

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ABSTRACT

In this study biodiesel was produced from palm oil using calcium oxide (CaO) as a heterogeneous catalyst. The waste chicken eggshell was applied as raw material for the preparation of heterogeneous catalyst in biodiesel production. Prior to use, the waste chicken eggshells were cleaned thoroughly with the running water and followed by distilled water and dried for 12 hr at 102°C, the calcium carbonate ($CaCO_3$) content in the waste egg shell was converted into calcium oxide (CaO) by calcining at 900°C for 4 hr. The effect of experimental variables namely reaction temperature, reaction time, methanol to oil ratio, and amount of catalyst were investigated.

Key words: Palm oil, Eggshell, Biodiesel, Optimization, CaO.

INTRODUCTION

Nowadays, the promising biofuel is biodiesel, which can be produced from edible vegetable oils like canola, soybean and corn found to be good as a diesel substitute [freedman] and non-edible oils such as animal fats, Jatrophacurcas, and waste oils such as soybean soap stock and yellow grease have been used in the production of biodiesel[1]. Biodiesel has shown great potential worldwide as a clean alternative fuel for diesel engines because of its reduced emission pollutants, sustainability, biodegradability, and usability in conventional diesel engines without significant modifications[2]. There are basically two types of catalyst that are used in the production of biodiesel namely homogenous and heterogeneous. The term of homogeneous means the catalysts are in the same phase with its reactants, whereas heterogeneous means that the catalysts are in a different phase from its reactant. Further homogenous catalyst can be categorized into homogenous bases and acids[3].

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In biodiesel production potassium hydroxide, sodium hydroxide, sodium methoxide are the commonly used basic catalysts production. An example of commonly used homogenous acid catalyst is sulphuric acids. Sulphuric acids is commonly used to esterify excess free fatty acids when the free fatty acid content is high. The disadvantages of using homogenous catalysts are that they cannot be recovered; intolerance of high free fatty acid (FFA) and also they require washing of biodiesel with pure water to remove the catalyst present. This results in wastewater generation, water contamination and loss of biodiesel as a result of water washing and this increases cost on municipal water treatment plants.

Heterogeneous catalysts can be classified into two main classes namely heterogeneous solid acid and heterogeneous base catalysts. Heterogeneous acid catalysts for example, heteropolyacid impregnated on different supports (silica, zirconia, alumina, and activated carbon), SO_4-ZrO_2 and WO_3-ZrO_2 as solid acid catalyst were indicated as catalysts for the transesterification of canola oil with methanol to produce biodiesel[4]. Unfortunately, these catalysts had drawbacks including longer reaction time and higher temperatures, which make them unfavorable. Heterogeneous solid base catalyst such as calcium oxide has some advantages over homogeneous catalyst because the catalyst can be reused (cost effective), has a tolerance of moisture and FFA (which allows the use of lower-quality used/waste oils), is inexpensive (obtainable from waste shells), has low methanol solubility, is noncorrosive and is environmental friendly. The main objective of this work was to study the feasibility of using calcium oxide from natural eggshell wastes to produce biodiesel from palm oil via a one-step alkali transesterification process.

EXPERIMENTAL

Material and methods

Palm oil (MW ~841 g/mol) containing 0.3-0.6% free fatty acid and less than 1% moisture content was obtained from local market. The chicken eggshell was collected as wastes from Restaurants in Chidambaram, Cuddalore District, 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.

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 4 hr[5]. In addition, with the increase in activation temperature, $CaCO_3$ completely transforms to CaO by evolving the CO_2.[6] 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[7]. Among the alkaline earth metal oxides, calcium oxide (CaO) is the promising heterogeneous catalyst for biodiesel production[8].

Production of biodiesel

A 500 mL 3-necked round bottom flask was used to produce biodiesel by transesterification reaction of palm oil with methanol. 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 thermometer for temperature indication. The speed of the magnetic stirrer was monitored[9]. The transesterification process parameters namely 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 5% of the mass of the oil. After a homogeneous mixture, palm oil is inserted into a flask and heated at a variable temperature 60, 65, 70^{o}C in 2, 3, 4 hrs of stirring. After that, the catalyst was screened by using a filter paper (0.7 μm) and the product was transferred to the separating funnel (decanter) and allowed to settle over night to enhance the 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. The bottom glycerol layer was discarded. The biodiesel yield was calculated based on the amount of biodiesel produced and amount of oil that was initially used.

RESULTS AND DISCUSSION

Effect of molar ratio of methanol to oil

The methanol to oil molar ratio is one of the most important variables affecting the conversion of Palm oil to biodiesel. The methyl ester purity in the product increases from 45 to 95% as the methanol to oil molar ratio increases from 5:1 to 11:1, and Fig. 1 shows the effect of methanol to oil ratio on purity of methyl ester in the product. The highest conversion (95%) was obtained at the molar ratio of 9:1 for 3 hr. However, further increases in the methanol to oil molar ratio, did not promote the conversion of biodiesel. It was understood that the higher methanol content dilutes the concentration of methoxide anion catalyst[10,11] Therefore, the optimal molar ratio of methanol and palm oil was to be 9:1.

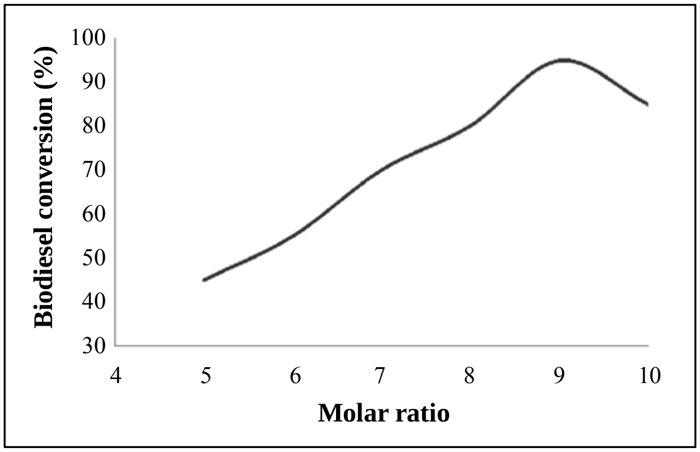

Fig. 1: Conversion of palm oil to biodiesel at different methanol to oil molar ratio (Reaction temp. 65°C, catalyst concentration 5% wt. of oil, reaction time 3 hr)

Effect of catalyst concentration on transesterification

The conversion of biodiesel from palm oil is severely affected by catalyst concentration. The effect of catalyst concentration on the conversion of biodiesel was investigated within the range of 4.0-11.0% CaO (based on the oil weight) and the results are illustrated in Fig. 2. With increasing of the amount of catalyst from 4.0% to 11.0%, 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 palm 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 conversion costs, Thus, the optimum amount of the catalyst was to be 5% CaO (on the basis of oil weight)[12-15].

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 catalyzed transesterification reaction. The reaction was conducted from 50-75°C temperature and the results are illustrated in Fig. 3. When the reaction temperature was less than 50^{o}C the conversion was less than 45%. With increasing the temperature from 50°C to 65°C the conversion of biodiesel increased rapidly. When the temperature was above 65^{0}C which is above the boiling point of methanol, the solvent vaporized and remained in the vapour phase in the reactor causing a reduction in the methanol in the reaction media[15]. It is indicating that the temperature of 65°C was enough for the transesterification of palm oil. The optimum temperature was to be 65°C.[16-18]

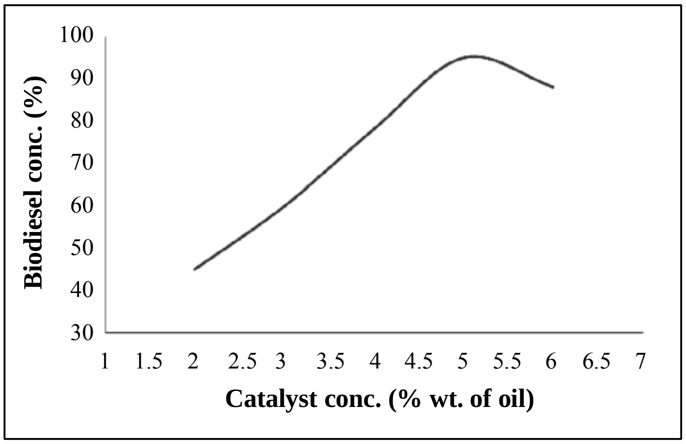

Fig. 2: Conversion of palm oil to biodiesel at different catalyst concentration (Reaction temp. 65^{o}C, methanol to oil ratio 9:1, Reaction time 3 hr, with vigorous stirring)

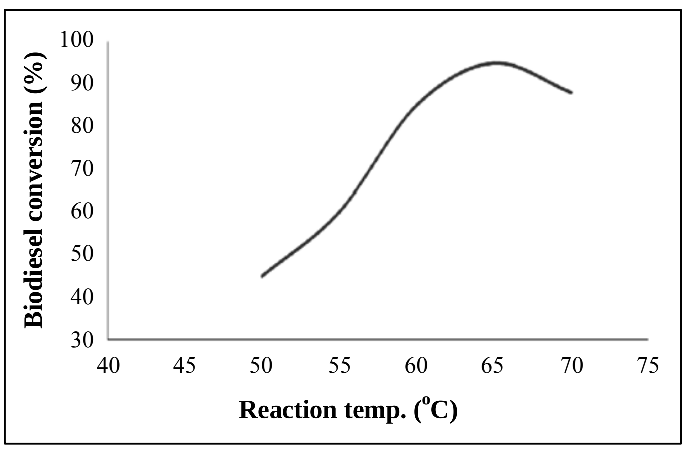

Fig. 3: Conversion of palm oil to biodiesel at different temperature (methanol to oil ratio 9:1, catalyst concentration 5% CaO, reaction time 3 hr, under reflux with vigorous stirring)

Effect of reaction time on transesterification

The effect of reaction time on the conversion of biodiesel at the catalysis of CaO was studied and the results are shown in Fig. 4. The reaction time was varied within the range from 0 to 4 hr. The reaction time for the transesterification increases with increases the conversion rate of biodiesel was observed with the increasing of time up to 3 hr, and there was no further increase in the yield. Therefore the optimum reaction time was 3 hr[15,19].

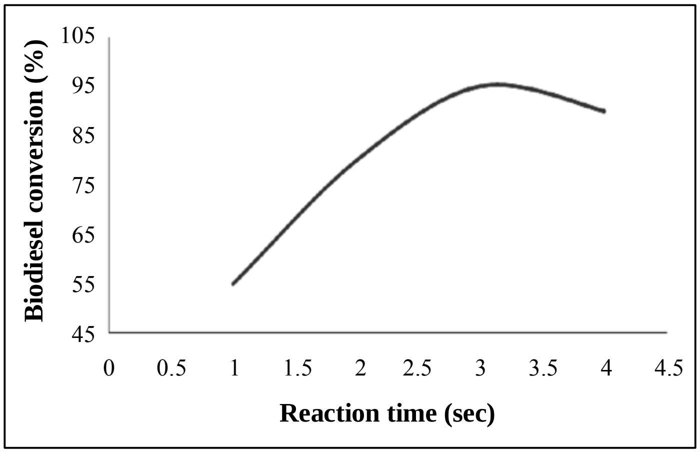

Fig. 4: Conversion of palm oil to biodiesel at different reaction time (methanol to oil ratio 9:1, reaction temperature 65^{o}C, catalyst concentration 5% CaO, under reflux with vigorous stirring)

CONCLUSION

The waste eggshells were used as main raw material, and as a catalyst for the production of biodiesel. This eggshell waste contains $CaCO_3$ under high temperature, which is converted to CaO after calcination at temperatures 900°C for 4 hr, and CaO was acknowledged as an effective heterogeneous catalyst for the transesterification of Palm oil and methanol. The effect of reaction conditions, which yield a conversion of 95% biodiesel, were reaction time 3 hr, reaction temperature 65°C, methanol to oil molar ratio 9:1, and catalyst concentration 5% wt of oil. The experimental results show that CaO catalyst had excellent activity and strength 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 palm oil to FAME.

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