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Original Article

UTILIZATION OF WASTE EGGSHELLS FOR PRODUCTION OF RENEWABLE CATALYST FOR TRANSESTERIFICATION

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ABSTRACT

Objective: This paper deals with the production of a nonconventional heterogeneous base catalyst from waste egg shells and comparison with conventional homogeneous and heterogeneous base catalysts like potassium hydroxide, sodium hydroxide, magnesium oxide and calcium oxide.

Methods: Three types of virgin oil were used to study the biodiesel yield. Trasesterification reaction was performed for the conversion to biodiesel. The biodiesel yield produced from palm oil, coconut oil and sunflower oil catalyzed with commercially available base catalysts was compared with prepared eggshell catalyst. Waste eggshells were calcined at 700 °C to 1000 °C for various time periods ranging from 2-4 h for the preparation of renewable catalyst after washing with deionizing water. The calcined waste eggshell catalyst was characterized using scanning electron microscope. The prepared catalyst was used for transesterification reaction.

Results: The yield of biodiesel using waste eggshell catalyst is comparable to conventional catalyst like sodium hydroxide with a yield of 95%. Eggshell catalyst has the advantage of reusability and does not require water washing steps. The eggshell catalyst was reused for four times before a decline in its activity. It exhibited lower reusability for coconut and palm oil because of leaching problems.

Conclusion: The prepared biodiesel was subjected to ASTM D6751 standard test to assess the fuel properties. The fuel properties was comparable to commercial diesel and hence it can be used in compression-ignition engines.

Keywords: Waste egg shell, Heterogeneous, Base catalyst, Virgin cooking oil, Biodiesel

INTRODUCTION

The homogeneous catalytic process has several disadvantages, i.e. producing a huge amount of wastewater for the purification of end product and the non-reusable nature [1]. The heterogeneous catalyst is discovered as one of the best options to solve the problems stated above [2]. A heterogeneous catalytic process can be simplified by the elimination of neutralization step of producing waste water [3]. Besides that, the heterogeneous catalyst can be separated easily and be reused. Hence, the capital cost is lower [4]. This can be overcome by optimizing the reaction parameters, to achieve maximum production of biodiesel with a minimum cost of raw material [5]. Solid base catalysts have been gaining increasing attention as substitutes for the highly pollutant liquid, homogeneous catalyst to produce biodiesel, as they generally do not generate large amounts of wastewater [6, 7]. The manufacturing cost of biodiesel using a calcium oxide (CaO) catalyst in a batch process with a plant capacity of 7260 tons/year, was lower by 15% compared to the cost which was incurred by using a potassium hydroxide catalyst [8].

Moreover, it was reported that CaO reduced heavy pollutants such as phenol and increased the formation of hydrocarbons and light products such as acetaldehyde, 2-butanone, and methanol. But the waste eggshell catalyst was plagued by problems like very low surface area, sensitivity to the presence of water, leaching of active sites by glycerol and competed with soap forming side reactions. To overcome such limitations, calcium oxide obtained from waste eggshells can be impregnated into supports such as silica, alumina or carbon materials such as activated carbon, nanoporous carbon, nanotubes, etc., [9]. Oxides of magnesium and calcium oxide have been tried as solid base catalyst owing to their easy availability, low cost and non-corrosive nature [10]. The research was also reported about the good performance of eggshells among the catalyst selection, in transesterification as chicken egg shell contains the highest calcium and larger surface area as compared to golden apple snail and Meretrixvenus shell [11]. The research was carried out with used eggshells to undergo calculations-hydration-dehydration treatment to obtain calcium oxide catalyst [12]. Eggshell calcined above 800 °C was found to be the most active with a biodiesel yield range of 97-99 %. This was attributed to the formation of crystalline CaO as the active phase used for the transesterification [13]. A research on emulsification of biodiesel with water to investigate its influence on the overall diesel engine was reported [14]. Very few research work has been carried on waste eggshell catalysts, and no comparison work has been done with commercially available catalysts. Hence, this research work compares the efficiency of produced waste eggshell catalyst with commercially available sodium hydroxide, potassium hydroxide, magnesium oxide and calcium oxide. The gas chromatography of biodiesel produced from palm oil catalyzed by the prepared waste eggshell catalyst is analyzed to determine the presence of fatty acid esters. Fuel properties was analyzed according to international biodiesel standard, ASTM (American Society of Testing Materials) D6751. Engine efficiency of prepared biodiesel was also compared with commercially available diesel.

MATERIALS AND METHODS

Materials

Waste eggshells were procured from canteen and bakery of Sathyabama University, Chennai. Palm oil, coconut oil and sunflower oil were three virgin oils used for the research work. Methanol, sodium hydroxide, potassium hydroxide, magnesium oxide and calcium oxide used for the experiment were of analytical grade.

Experimental

The procured eggshells were washed with deionized water to remove the impurities attached to the shells. The shells were dried at 100 °C for 24 h. The eggshells were calcined at a high temperature ranging from 700-1000 °C for 2,3 and 4 h. The calcined eggshells were transesterified with palm oil, coconut oil and sunflower oil with methanol as cited in the literature [4, 6, 9]. The molar ratio of oil: alcohol was fixed at 1:6 for all experiments. Coconut oil and sunflower oil were directly transesterified since their free fatty acid content (FFA) was less than 2%. Since the FFA content was higher than 2% of palm oil, the oil was esterified with methanol to reduce

the FFA % and then tranesterified to biodiesel. The catalyst was dissolved in methanol and stirred for 20 min prior to transesterification to ensure the complete dissolution of homogeneous catalyst pellets. A premixed mixture of catalyst and alcohol is kept in a round bottom flask fitted with a condenser to maintain a uniform temperature throughout the process. Transesterification is the reaction between triacylglycerols and alcohol in the catalyst presence to yield fatty acid alkyl esters. This is mainly performed to reduce the viscosity of parent oil. To the reaction set up, the waste eggshell catalyst is added to palm oil, coconut oil and sunflower oil for separate experimental runs. The same protocol was followed for homogeneous base catalysts like potassium hydroxide,sodium hydroxide and heterogeneous base catalysts like magnesium oxide and calcium oxide. Since there is a possibility of soap formation,water washing is required for homogeneous base catalysts. The first wash was given with 5 wt% warm water followed by 5 wt% cold water. The resulting mixture was poured into a separating funnel and the biodiesel layer was separated from the foamy layer. The obtained biodiesel was then oven dried at 60 °C for 14 h and stored [5,11]. The heterogeneous base catalyst was recovered after each experiment by filtration and then oven dried. All experiments were triplicated and their reproducibility was±4%. The obtained biodiesel was characterized according to Ameican Society of Testing Materials.

The Yield of the biodiesel was calculated by the following equation

Biodiesel Yield (%) = (Weight of biodiesel/weight of oil) x100 [1]

Test procedure for determining fuel properties

Biodiesel has to be tested for its fuel properties according to a universal standard to be accepted for engine applications. The biodiesel was tested according to ASTM D6751 standards. ASTM D6751 specifies various test methods which the biodiesel should satisfy,to be acceptable to be used in engines.

Density

Density can be found from weighing an empty specific gravity bottle initially, and the weight was noted as W_1. The specific gravity bottle was weighed with water, and the weight was noted as W_2. Biodiesel was filled in the bottle and weight was noted as W_3.

$$\text{Specific gravity} = (W_3\text{-}W_{1)/}(W_2\text{-}W_1) \quad [2]$$

Density of oil = Specific gravity x density of water

Kinematic viscosity

The viscosity of the oil samples was found by using Ostwald Viscometer, which comprises of a capillary through which the samples are allowed to flow and the time measurements were made. The density of the oil samples was determined using a specific gravity bottle. Time taken for the reference liquid (water) to travel down the capillary was noted. The viscometer was then filled with oil samples whose viscosity were to be determined. The time noted for the oil sample to travel down the capillary was noted down for all the oils separately.

Flashpoint

The flash point of the oil samples was determined using a Penskey Open Cup apparatus. After thoroughly cleaning the testing apparatus and cup, the test cup was filled to the level indicated by the indicator mark. With the heating device set to the proper level, the thermometer was inserted in the testing apparatus and the stirring device was attached. The initial temperature was 70°F. The first oil sample was heated at a rate of 9-11 °F per minute. The rate of temperature increase was carefully controlled so the flash point could be accurately measured. After the test flame had been lighted, it was applied to the specimen at 4-5 second intervals after the temperature had reached 90 °F. The specimen was continued to be heated, and the flash point was then observed.

Calculated cetane index

Calculated Cetane Index (CCI) is an alternate to the cetane number. It is calculated from the distillation range and specific gravity of the fuel.

Calculated cetane index =-420.34+0.016 G^2+0.192 G log M+65.01 $(\log M)^2$-0.0001809 M^2.

G = API Degrees at 60 °F

M = D86 Temperature @ 50% volume, in °F

Acid value

5 g of sample was weighed accurately and mixed with 50 ml of ethyl alcohol. The mixture was heated over a water bath for 30 min. After cooling, few drops of phenolphthalein indicator was added. It was titrated with potassium hydroxide (KOH) solution until faint permanent pink color appears at the end point.

Calorific value

Bomb calorimeter was used to measure the calorific value of the fuel. A known quantity of fuel sample was added in a crucible. Electricity was passed through crucible and fuel sample was burned in the presence of oxygen. The final steady state temperature of the water was noted.

$$\text{Calorific value of fuel} = (m_1+m_2) \times (Tc+T_{1}\text{-}T_{2}) \times C_w/mf$$

Where,

m_1 and m_2 are masses of water in the copper calorimeter and water equivalent of bomb calorimeter respectively.

mf is mass of fuel sample whose calorific value is to be determined.

T_1 and T_2 are the final and initial temperature of the water sample. Tc is temperature correction for radiation losses.

Cw is specific heat of water

RESULTS AND DISCUSSION

The biodiesel yield obtained from palm oil was higher for sodium hydroxide catalyst followed by potassium hydroxide, magnesium oxide, commercial calcium oxide and eggshell catalyst respectively as illustrated in fig. 1. This is in agreement with earlier studies. The biodiesel yield from coconut oil was the highest, using magnesium oxide as the catalyst followed by sodium hydroxide, potassium hydroxide, commercial calcium oxide and eggshell catalyst respectively as illustrated in fig. 1. From fig. 1, it can also be inferred that the biodiesel yield from sunflower oil was the highest using sodium hydroxide and eggshell catalyst. Magnesium oxide catalyst gave the least yield for sunflower oil biodiesel.

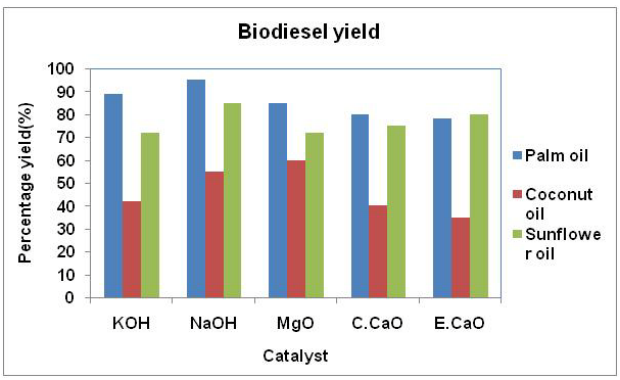

Fig. 1: Biodiesel yield for various feedstocks (100 ml of oil)

Fig. 2 represents the biodiesel yield for the various catalysts for palm, coconut and sunflower oils. The major advantage of heterogeneous catalyst is that it can be reused. The eggshell catalyst was recovered by filtering and then activated in the oven for one hour. Fig. 3 shows the scanning electron microscopy of the prepared waste eggshell catalyst. It can be inferred from the image that the pores are well formed and indicates an amorphous nature of catalyst particles. Fig. 4 represents the reusability of eggshell catalyst for

palm, coconut and sunflower oils. Reusability was the lowest for palm oil and was the highest for sunflower biodiesel. For palm oil, the yield percentage is seen to decrease gradually with the number of runtimes. As shown in the graph the highest yield percentage for palm oil was about 75% for the first run followed by the second run, giving a yield percentage of 30% after which it could not be used because of leaching problems. For sunflower oil, the yield percentage was seen to have a steep decrease with the number of runtimes. As shown in the graph the highest yield percentage for sunflower oil obtained for the first run was approximately 80%, which then drops down to 50% for the second run and then reaches 22% for the third run and finally approaches to 7% for the fourth run. On an average, waste eggshells can be recycled for 3-4 times.

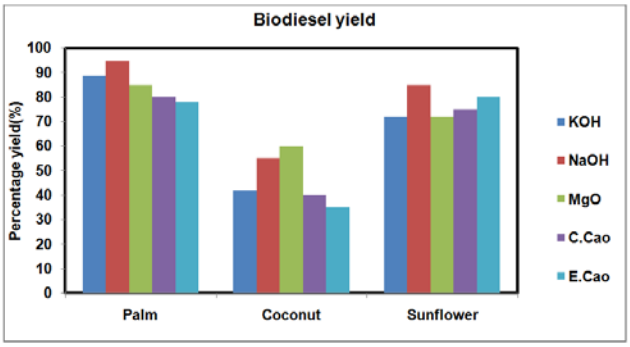

Fig. 2: Biodiesel yield for heterogeneous base catalyst (5 wt % of catalyst)

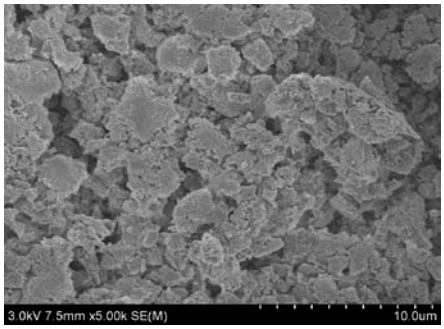

Fig. 3: SEM image of waste eggshell catalyst

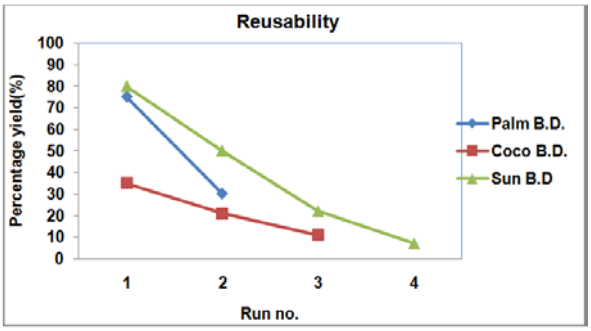

Fig. 4: Biodiesel yield for heterogeneous base catalyst (100 ml of oil)

Table 1: Fuel properties of eggshell catalyzed biodiesel

Property	Sunflower biodiesel	Palm biodiesel	Coconut biodiesel	Conventional diesel
Density (kg/l)	0.872	0.88	0.75	0.855
Kinematic viscosity (CSt)	4.6	5.7	3.2	3.66
Flash point (°C)	102	124	97	85
Calorific value (KJ/Kg)	40.51	33.5	42.7	50
Calculated cetane index	52	65	36	45
Acid value (mgKOH/g)	0.15	0.2	0.1	0.4

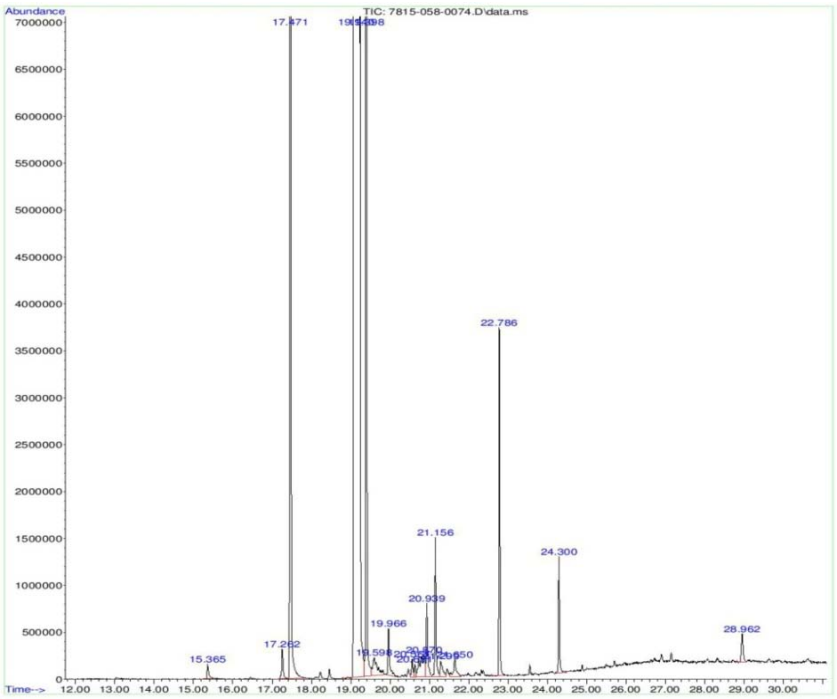

Fig. 5: GC-MS of palm biodiesel catalyzed by waste eggshells

Table 1 represents the fuel properties obtained by using an eggshell catalyst for sunflower oil, coconut and palm oil with a comparison to conventional diesel. Biodiesel density was slightly higher than conventional diesel fuel, and this allows the use of splash blending [15]. Kinematic Viscosity is an important property of all fuel oils since it results in a negative impact on fuel injection system performance. Since the viscosity of biodiesel catalysed using waste eggshells was within the range of ASTM it is ideal to be used as fuels in diesel engines. Acid number of biodiesel should be lower than 0.50 mg KOH/g. Acid value of biodiesel as shown in table 1 was found to be in the permissible limits of ASTM D6751. The flash point of a fuel is defined as the temperature at which it will ignite when exposed to a flame or spark. Since the flash point of biodiesel was higher, blending with conventional diesel is suggested. Thus, in storage, biodiesel, and its blends are safer than conventional diesel. Fig. 5 represents the gas chromatograph of biodiesel catalyzed by waste eggshells, which indicates the presence of the predominant fatty acids which influence the characteristics of the biodiesel. It was composed of saturated and unsaturated fatty acids with 10-24 carbon atoms. Unsaturated fatty acids lead to polymerization of the fuel, which leads to gum thickening which might clog the fuel filters. The major fatty acids present are linoleic acid, oleic acid, lignoceric acid, stearic acid and palmitic acid along with other fatty acids. Fig. 5 shows the variation of total fuel consumption with brake power for biodiesel and conventional diesel. Accurate measurement of fuel consumption is very important in engine testing work. The fuel consumption of biodiesel was higher than that of conventional diesel fuel. Specific Fuel Consumption (SFC) indicates the efficiency of the engine in using the fuel supplied to produce work. Minimum fuel for same workload is desirable. Fig. 6 shows the SFC of biodiesel and conventional diesel. The specific fuel consumption increases and then decreases for both with the higher trend for biodiesel, which can be contributed to low calorific value.

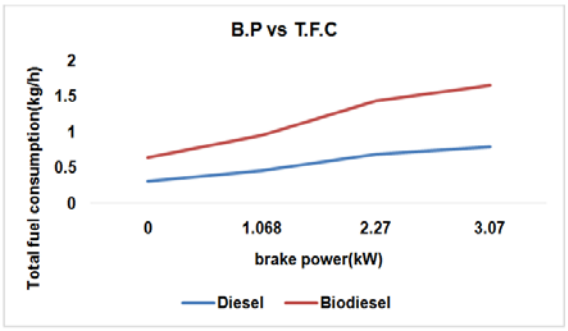

Fig. 6: Variation of brake power with total fuel consumption

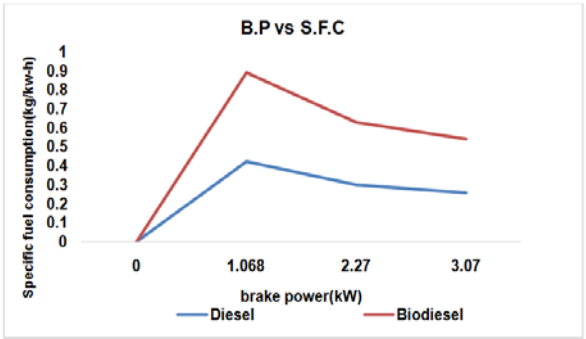

Fig. 7: Variation of brake power with specific fuel consumption

CONCLUSION

From the experimental results, it can be concluded that waste eggshells can be calcined and activated to produce a catalyst which is suitable for biodiesel transesterification. This was evident from the gas chromatograph analysis. The calcined waste eggshells can be reused up to four runs. The engine efficiency in terms of total fuel consumption and specific fuel consumption was comparable to conventional diesel. The fuel properties analyzed according to ASTM D6751 was also good in comparison to conventional diesel. Hence, it can be concluded that the utilization of waste eggshells as a catalyst makes biodiesel commercialization feasible and cost effective.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest with persons or organizations

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