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Integrated Approach for Enhanced Biodiesel Production; Optimization of biodiesel production with high FFA coconut oil and valorisation of By-products

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Abstract- Biodiesel is not cost-effective due to the high price of fixed oils. In contrast, underutilized vegetable oils from leftover "*poonac*" and sludge may be an alternative. However, high free fatty acid (FFA) needs to be neutralized by acid-catalyzed transesterification. Oil samples were collected from three different oil mills in the western province and then composited. The free fatty acid of the oil was determined first followed by pretreatment of 1000 ml sample and then base-catalyzed transesterification was done as per standard protocol. Biodiesel so produced was tested as per ASTM D6751. About 30% v/v crude glycerin is produced as a byproduct during the process which was further neutralized, physically refined and then used for product development. FFA was 7.2 %.v/v, total acid number = 0.53 mg KOH/g, viscosity at 40 ^{o}C/CST = 5.077, Cloud point / ^{o}C = +10, total Cu corrosion test = 1a, water and sediment (v/v %) = <0.01, flash point/ ^{o}C = 123.0. From the results, it was evident that most of the parameters were within the standard values except for total acid number 0.53 mg KOH/g. Industrially, glycerin is used after distillation which is not cost effective. However, physical treatment was good enough to use glycerin for industrial applications such as biodegradable carwash & surface cleaners as cost-effective consumer products.

Keywords- ASTM, Biodiesel, High FFA, Catalyst, Transesterification

I. INTRODUCTION

To meet its needs for transportation fuel, Sri Lanka is entirely dependent on imported petroleum products, with diesel being the most commonly used petroleum product in the transportation sector. High inflation in consumer goods is a result of rising petroleum product prices, including diesel. Biodiesel can be produced using various types of vegetable oils such as palm oil, castor oil, coconut oil, etc., but per litre, the cost is high and also, due to demand in the food industry such oils are inappropriate for biodiesel production. In contrast, underutilized fixed oils such as "*Polkudu thel*", "*Sludge oil*", and "*Majan oil*" from oil expellers are available and can be best utilized for biodiesel cost-effectively due to underutilization. In contrast, High Free Fatty Acid containing coconut oil is produced due to various reasons in the production process of coconut oil. For example "*Polkudu Thel*" yields above 30 % of fixed oil which is underutilized. Approximately 10 tons of such underutilized coconut oil available in Sri Lanka can be value-added to produce biodiesel for the existing energy crisis which only used in diesel engines, but also can be used for generators, tractors, diesel three-wheelers, etc.

Crude glycerin derived from biodiesel is impure and has low economic value. In transesterification processes (Alkali-catalyzed transesterification, Acid-catalyzed transesterification), derived Crude Glycerol typically has a dark brown colour with a high pH (The colour and the pH can be slightly varied with the type of the alcohol and transesterification process). Crude glycerin derived from biodiesel production contains impurities such as soap, alcohol, salts, water, fatty acid, ethyl ester, triglycerides, and ash. Therefore, it cannot be used directly for industrial use without doing a purification process.

The purification process can be done by several methods; such as a double distillation, ion exchange resin, membrane separation technology, and acidification, followed by neutralization and solvent extraction. However, the process is not cost-effective for small-scale producers. In contrast, Crude glycerin can be used as industrial value-added, products after a simple purification process. The major objective is to add value to crude glycerin obtained from biodiesel production as a biodegradable car wash, surface cleaners and detergents.

II. MATERIALS AND METHODOLOGY

A. *Materials*

A sample (around 10 litres) of High Free Fatty Acid containing coconut oil was purchased from coconut oil mills (western province / Sri Lanka). Isopropanol and potassium hydroxide were obtained from LOBA CHEMIE (India), and ethanol (Honeywell, Poland). Phenolphthalein, concentrated sulfuric acid/H_2SO_4 (SRL Pvt. Ltd), Crude glycerin derived from biodiesel**,** distilled water, overhead stir (VELP, Scientifica LS), heater (Bibby, HB502), Tonsil, cotton wool, centrifuge (Centurion Scientific- K3 series), pH meter (Eutech pH 700) and laboratory grade glassware, chemicals employed were analytical grade.

B. *Methodology*

1) *FFA% determination of the oil*

The oil's FFA% equals half of its acid value (AV). The oil's AV was calculated in accordance with ASTM standards.

2) *Acid esterification (Pre-treatment)*

This is a pretreatment step to lower the FFA content of the oil to a level that is close to 2%. The required amount of con. H_2SO_4 was added as an acid catalyst to a significant amount of ethanol before the mixture was added to oil with a high FFA content. The oil-ethanol mixture was then preheated to 50–55ºC and the temperature was maintained at the above value for the reaction to occur with mixing. The reaction was then allowed to continue for 24 hours at room temperature. The top layer, which contains ethanol and water, was discarded after the bottom layer had been separated after 24 hours. The separated bottom layer's FFA content was measured. Alkaline esterification was used to produce biodiesel if the FFA content was less than 2%; otherwise, the above process was repeated until the FFA content was less than 2%. However, for the present study ethanol was used in place of methanol. (P.R.A.U.Sampath, 2019)

3) *The amount of ethanol required*

In order to examine the impact of the amount of ethanol in the FFA reduction, different amounts of ethanol were used in this study. The amounts chosen ranged from 2.5 g ethanol to 3.0 g ethanol to 1 g of FFA, depending on how much FFA was present. In a beaker, 100 ml of coconut oil containing high levels of free fatty acids (with an initial FFA value of 7.2%) was heated to a temperature between 50 and 55 ºC. The above amounts of ethanol were combined with 1.15 g of con. H2SO4 (0.05 g con. H_2SO_4/ 1 g of FFA in oil), which was then added to the heated oil. For 20 minutes, the heating process continued. The mixture was left to settle for 24 hours after 20 minutes (Fatah H. Alhassana & Yoshimitsu Uemuraa 2016)

4) *The reaction time*

In this study, different heating and mixing times (10, 20, 30, and 60 minutes) were used while maintaining the same catalyst concentration and heating temperature as in 2.2 The amount of methanol used was the same as in 2.2, and the amount of H_2SO_4 used remained constant at 0.05 g/1 g of FFA in oil.

5) *Alkaline esterification*

The oil is ready for the production of biodiesel when the FFA content is decreased to a level of about 2%. Triglycerides are transesterified to mono esters in this step. For this step, oil that has done pretreatment in accordance with 2.2 was used (João Felipe G. Oliveira 2010).

6) *Potassium ethoxide preparation*

The catalyst used for the alkaline esterification reaction is KOH. A titration was used to determine the 0.78 g of KOH needed for the reaction (website 1). Typically, 24% of the volume of oil is needed for the reaction's stoichiometric amount of ethanol Fatah H. Alhassana & Yoshimitsu Uemuraa (2016).

7) *Production steps of ethyl ester*

The ethoxide was added to heated pretreated oil after it had been heated to a temperature of 50 to 55 ºC. A glass beaker was used to continue heating and mixing for an additional 60 minutes. The top layer, which contains the ethyl ester of the coconut oil, was then separated after the mixture had been allowed to settle at room temperature for 24 hours. When the pH of this ethyl ester was measured, it was reported as 7.

8) Biodiesel testing

According to the ASTM D6751, total acid number, viscosity, cloud point, copper corrosion, flash point, water and sediment were tested (Website 1,2,3).

C. Crude Glycerin purification

1) Sulfuric acid preparation

2N Sulfuric acid was prepared as follows; 500ml of distilled water was added into a 1l volumetric flask. Then 54.35ml of concentrated H_2SO_4 was measured from a measuring cylinder and then conc. H_2SO_4 was slowly added to the measured distilled water. Finally, the volumetric flask was topped up with distilled water until it reached 1l.

2) Acid treatment

1kg of crude glycerin derived from biodiesel was added into a 2000ml beaker. The required amount of 2N H_2SO_4 solution was added in to that beaker containing glycerin. Then the vessel was heated at 80 - 100 °C temperature in a water bath. When the glycerol melted, the mixture was stirred for 10 minutes under 100 rpm. Then the mixture was added into a separating funnel and allowed to separate overnight. The bottom layer containing salt and water was removed and the top layer containing liquid glycerin was used for further purification processes by gravity filtration by "Tonsil".

3) Glycerin filtration

A funnel was placed on a stand and placed a cotton wool layer at the bottom of the funnel. "Tonsil", an oil-purifying clay (50 g) was added on the cotton wool layer. Then slowly add the liquid glycerin into the funnel containing "Tonsil". Then allowed to filter overnight.

4) Glycerin centrifugation

The filtered glycerin was centrifuged for 10 minutes and then, the purified crude glycerin was tested for the purity of glycerol, magnesium and calcium ions by ICP-MS after microwave digestion. Free caustic alkali was analyzed titrimetrically (Fernando D. Pitta, Anabela M. Domingosc, A.A. Chivanga Barros 2019 & César A.G. Quispe, Christian J.R. Coronado, João A. Carvalho Jr, 2013).

III. RESULTS

A. Test results of optimized ethyl ester

After testing the total acid number was 0.53 mg KOH/g, viscosity at 40 ^oC/CST = 5.077, Cloud point / ^oC = +10. The Cu corrosion test result was 1a, and finally the water and sediment (v/v %) = <0.01 (max) and the flash point/ ^oC = 123.0. The comparison of the test results with standard biodiesel and petroleum diesel (Table.1).

B. Test results of crude glycerin

The Glycerol content was 86.5% in the purified crude glycerin. Water content = 2.5% v/v, pH value = 6 – 8, and free caustic alkali was not detected. In the results it scopes 4.0% of ethyl ester, calcium = 54.0 mg/kg, magnesium = 10.7 mg/kg and the specific gravity was 0.9088. The specifications of the test results with standard crude glycerin and purified crude glycerin (Table.2).

IV. DISCUSSION

The High Free Fatty Acid Containing Coconut oil which was subjected for the testing had a 7.2 % level of free fatty acids. The effects of various reaction parameters such as temperature, ethanol content, catalyst concentration, and reaction time for the transesterification process with ethanol were assessed.

When used as a fuel, biodiesel with a lower viscosity has greater quality and performs better in engines. The results demonstrated that the ethyl esters made from coconut oil with a high free fatty acid content matched the standard biodiesel viscosity parameter required for viscosity.

To prevent unexpected fires, a fuel with such an elevated flash point is preferable for transportation of fuels. Biodiesel typically has a higher flash point than petroleum diesel. In a similar way, Ethyl ester has a high flash point.
The weight of potassium hydroxide (in mg) needed to neutralize all of the acidic species (like fatty acids) present in one gram of biodiesel is used to calculate the total acid number.

From the results, it was revealed that the pH of the glycerin was within the standard glycerin. Moisture content was about 2.5% v/v and specific gravity was 0.9088 respectively. However, standard crude glycerin parameters have not been considered. Since, detergent products should have enough surfactant properties ions such as, calcium and magnesium may interfere with such activity. Therefore, such ion content was determined. Finally, free caustic alkali was determined in order to check the product to see whether the product had been neutralized. Details of the analysis is in Table 2.

V. CONCLUSION

From the above results, it can be concluded that the underutilized coconut oil; sludge oil, used cooking oil, and edible cooking oil which has developed high free fatty acid due to long storage, and rancidity can be used in the production of biodiesel in cost-effective manner. However, further studies may be needed before commercialization. Also, it was revealed that the pH of purified glycerin is near neutral. Also free caustic alkali content was minimum. Though calcium and magnesium ion content was slightly higher which can be used in surfactant formulations after adding an ion chelating agent such as EDTA. Therefore, it is recommended to use purified glycerin from biodiesel production as a cost-effective raw material in car wash and surface cleaning detergent products.

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Table 1. Properties of ethyl ester, standard biodiesel and petroleum diesel

Properties	Ethyl ester	Standard Biodiesel	Petroleum diesel
Total acid number, mg KOH/ g	0.53	0.50	0.158
Viscosity at 40 ^{o}C/CST	5.077	1.9 – 6.0	1.3 - 4.1
Clod point/ ^{o}C	+10	-3 to 12	-15 to 5
Cu corrosion	1a	-	-
Water and sediment (v/v %),max	<0.01	0.050	0.161
Flash point/ ^{o}C	123.0	100 - 170	60 - 80

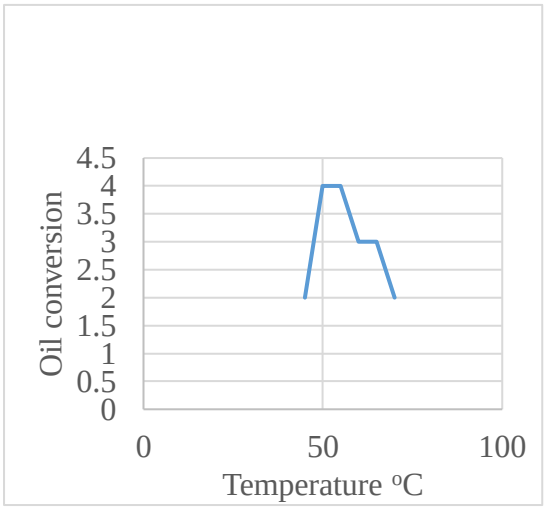

Figure 1. Effect of Temperature of the reaction at 1 hour, catalyst concentration of 0.6 %, alcohol to oil molar ratio of 4.1:1 and stirring speed of 300 rounds per minute (rpm).

The effects of temperature on fuel conversion are illustrated with the molar ratio of ethanol to sludge oil (4.1:1), 0.6 % potassium hydroxide, time (1 hour), and stirring speed (300 rpm). According to the results, the conversion efficiency increased at 50 and 55 °C. The conversion rate dropped when the temperature of the reaction was increased to 70 °C, which may have been caused by the loss of ethanol.

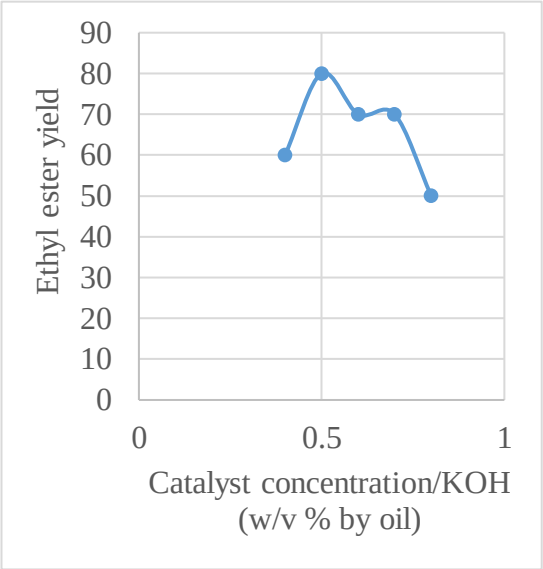

Figure 2. Effect of catalyst concentration at 1 hour, ethyl alcohol/oil molar ratio of 4:1, 50-55^{o}C temperature of the reaction and stirring speed of 300 rpm.

The minimum concentration of potassium hydroxide (0.4 %) proved unable to push the transesterification towards completion, as is evident in figure 2. Similarly, raising the potassium hydroxide content had no positive effect on the ethyl ester yield. In a similar manner, the ethyl ester yield reduced when the concentration of potassium hydroxide reached to more than 0.8 %.

Table 2. Specifications of standard crude glycerin and purified crude glycerin

Specification	Standard crude glycerin	Purified crude glycerin (test results)
pH value	4 – 9	6 – 8
Water content	13.0% max	2.5% v/v
Glycerol content	80.0% min	86.5%
Free caustic alkali	NA	Not detected
Ethyl ester	NA	4.0%
Specific gravity	NA	0.9088
Calcium	NA	54.0 mg/kg
Magnesium	NA	10.7 mg/kg