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Biofuel Production from Locally Sourced Roselle *(Hibiscus Sabdariffa* L.*)* Seed Oil Using Transesterification Process

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Abstract

As a solution to the decreasing stocks of fossil fuels and the environmental unfriendliness arising from its combustion, alternative fuels from natural sources are emerging. Biofuel has drawn considerable attention as a substitute fuel for diesel engines among these various potential resources as it is renewable, non-toxic, eco-friendly etc. This research assessed the production of biofuel from crude roselle oil. Using solvent extraction technique, oil was obtained from roselle seed and the properties evaluated. For this purpose, N-hexane and pet-ether solutions were used. The extracted oil was transesterified. The transesterification reaction was performed at a 6:1 methanol / oil molar ratio, with a catalyst of 1 percent (w / w) CaO / ZnO. The crude roselle oil obtained for use in the production of biofuels was clear, viscous and yellowish in colour, and the oil yield was 13.56 %. The result of the transesterification reaction was a transparent yellowish colour liquid (biofuel) and the percentage yield was 52.77 %. The flash point of 206 °C, pour point of -3 °C, cloud point of 4°C, cetane number of 5, fire point of 210 °C, specific gravity of 0.895 obtained at 29 °C, kinematic viscosity of 4.56 mm^2/s, Iodine Value of 0.39 $gI_2/100g$, saponification value of 0.16 MgKOH/g, acid value of 0.42 MgKOH/g and density of 0.874 g/cm^3 were all within the ASTM D6751 specification for biodiesel fuel. Roselle oil methyl ester was found to have good fuel quality and has potential to fuel a diesel powered engine.

Keywords: Crude roselle oil; transesterification; methyl esters; biofuel

1.0 INTRODUCTION

As a solution to the diminishing stocks of fossil fuels and the ecological unfriendliness emanating from the burning of fossil fuels, alternative fuels from local sources are evolving. Biofuel has drawn substantial attention as a substitute fuel for diesel powered engines among these different probable resources since it is renewable, biodegradable, non-inflammable and non-toxic, environmentally suitable and can be produced locally [1].

According to [2], biofuel is an animal or vegetable oil-based diesel fuel that burns without the emission of much soot, carbon IV oxide and particulate matter. As a fuel, the properties of biodiesel are better, and it is more biodegradable than fossil diesel [3]. It is also a carbon-neutral source of fuel and is progressively becoming widespread. However, the use of high-viscous oils as fuel results in adverse effects on the method of combustion [4] therefore, to be consistent with contemporary engines, these oils must be derivatized. One way of accomplishing this objective is to convert big, branched triglycerides into smaller, straight-chain monoalkyl ester molecules through a method called transesterification [5].

Transesterification is the chemical reaction whereby glycerin is removed from the triglyceride (vegetable oil) by reacting it with an alcohol such as methanol, ethanol, butanol and propanol in the presence of a catalyst, to form an ester (biodiesel) [6-9]. Vegetable oil transesterification is a relatively simple reaction that produces glycerol as the only by-product. A catalyst is usually needed because the transesterification process is a very slow reaction, and can be achieved majorly by acid

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catalysis or base catalysis [1]. Biofuel can be produced from extensive variety of oilseed plants and animal fats. Edible and non-edible oils can be used for biofuel production. It is also possible to use oil from Jatropha, melon, soybean, sugar cane and "used oil" to produce biofuel [5].

As a prospective feedstock, a new contender of *Hibiscus specie* crops is evolving: roselle seed oil. A native tropical African plant, Roselle (*Hibiscus sabdariffa* L.), is a member of the Malvaceae family which is known by many common names especially in tropical countries such as *Zobo, Dawadawa, Bosto*, Roselle etc. It is an important annual crop successfully grown in tropical and sub-tropical climates. The most commonly consumed part of the plant is the calyx (sepals) surrounding the fruit (capsule) [10]. The only known product of this crop in Nigeria at the moment is the non-alcoholic beverage drink called *Zobo* that people use to rejuvenate themselves regardless of era, ethnic and religious background [11].

The seed has been discovered to be a source of oil with characteristics akin to that of crude olive oil but the plants from which useful oil could be obtained are wasted in their cultivation centres after which the farmer might have taken the quantity required for calyce production for the next planting period [11]. Several studies have already been conducted on roselle seed oil. In a commercial context, however, this oil is not currently widely used in Nigeria, with comparatively few competing of medicinal and food uses, a fact that prompted the evaluation of its potential for biofuel production.

2.0 MATERIALS AND METHODS

In this research, sample of roselle (*Hibiscus sabdariffa* L) seeds as shown in Figure 1 were obtained from a local market in Nigeria. Foreign materials and dirt lodging within the seeds were removed and air dried. All reagents used in this research were analytical grade and were used without further purification.

Figure 1: Roselle seed sample

2.1 Roselle seed oil production

2.1.1 Oil extraction

The oil was extracted using the cold maceration-solvent extraction method. 1000 g of *Hibiscus sabdariffa* L. was weighed and blended using an electric blending machine (National Model MX-915C, Japan) to a coarse particle size in order to increase its surface area, as particle size has an effect on the yield of oil as reported by [12]. The blended *Hibiscus sabdariffa* L. was soaked in 1 litre of Hexane and 1 litre of Ether solutions. The mixture was then kept for 24 hours for settling after which the oil-solvent mixture was decanted. The decanted mixture was concentrated at a temperature of 65 ºC in a rotary evaporator to release n-Hexane and Ether solutions. After filtration, the resulting biomass was collected and dried. The oil yield as shown in figure 2 was evaluated as the ratio of the weight of oil extracted to the weight of the Roselle oilseed powder sample. This is mathematically expressed as:

$$\%\ oil\ yield = \frac{weight\ in\ grams\ of\ oil\ extracted(g)}{weight\ in\ gram\ of\ oil\ sample(g)} \tag{1}$$

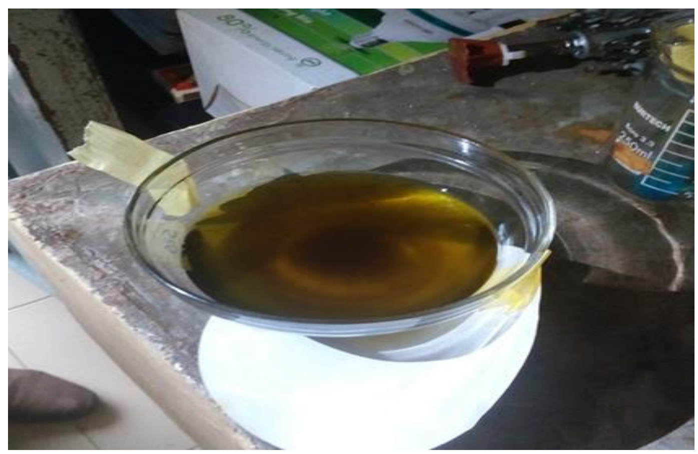

Figure 2: Crude Roselle Oil

2.2 Biodiesel production

The flow chart showing the unit operation involved in biofuel production is as shown in Figure 3.

2.3 Mixing of catalyst and methanol

A heterogeneous catalyst was employed in this reaction. For adequate dissolution of the catalyst, 1 g of ZnO and CaO were added to 60 ml of methanol and mixed thoroughly for 5 minutes.

2.3.1. Transesterification

Transesterification is the process in which nonedible oil is allowed to chemically react with alcohol.

The premixed mixture of catalyst with methanol was poured into the roselle oil in a conical flask in ratio 6:1:1 (methanol: catalyst: oil). A magnetic stirrer regulatory hotplate was then used to stir and heat the conical flask containing the solution for 60 minutes at a temperature of 60 ºC.

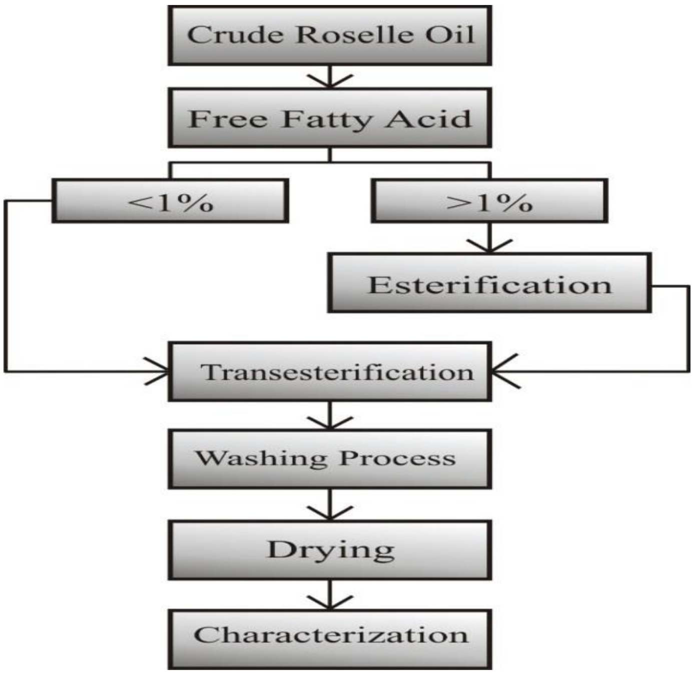

Figure 3: Flow chart of unit operations for biofuel production

2.3.2. Settling

After stirring the solution for 60 minutes, it was allowed to settle for 24 hours under gravity in a flask separator. Two distinct layers were clearly seen. The bottom layer comprised of unreacted oil, glycerin, catalyst and impurities. The top layer was made up of biofuel and excess alcohol.

2.3.3. Separation of biodiesel

The biofuel was separated from the residue layer consisting of glycerin, excess alcohol, catalyst, impurities and remnants of unreacted oil by flask separator.

2.3.4. Washing

After separation process, the roselle methyl ester was mixed and washed with warm distilled water to remove contaminants and allowed to settle under gravity. This was performed until the transparent water in the separating funnel was seen below the biofuel.

2.3.5. Drying

By placing it on a hot plate, the washed sample was dried, and excess water was removed from the biofuel.

2.3.6. Storage

The biofuel produced was measured using a measuring cylinder which was then stored for evaluation.

2.4 Evaluation of biofuel yield

The percentage yield of methyl ester was evaluated as the proportion of biofuel weight to roselle oil weight used.

$$\text{Methyl ester yield} = \frac{\text{weight of methyl ester produced } (g)}{\text{weight of oil } (g)} \quad (2)$$

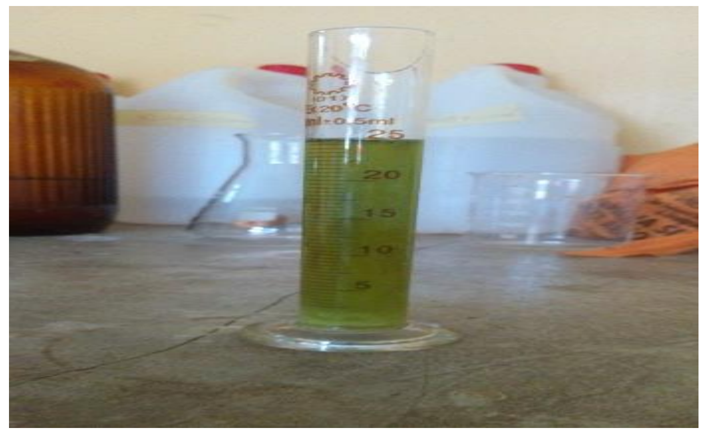

Figure 4: Roselle Methyl Ester

2.4.1 Determination of Some Roselle Biofuel Properties

Some of the fuel properties were determined at the Department of Petroleum Engineering, University of Ibadan, Ibadan, Nigeria, using the conventional techniques of the American Society for Testing and Materials (ASTM 6751). Cannon-Fenske Capillary Viscometer tube was used to determine the kinematic viscosity of the oil samples using the technique in ASTM D445. Based on the method described in ASTM D1298, the specific gravity of the fuel samples was evaluated using a pycnometer. The flash point of the oil specimens was determined by heating the fuel sample in a stirred container and passing a flame over the fluid surface using the Pensky Martens flash point closed device as outlined in ASTM D93. As defined in ASTM D97, by cooling the sample at a defined pace, the pour point of the fuel sample was determined and the sample was examined for flow at 3 ºC intervals. The lowest sample motion temperature was noted as the pour point. Also, as described in ASTM D2500, the fuel sample cloud point was evaluated by visually checking for a haze in the normally clear fuel, while the fuel was cooled under carefully controlled conditions. The acid value was determined using a pH-sensitive electrode according to the ASTM D 664 test method. The oil sample's saponification value, iodine value, and acid value were determined using the technique outlined in the formal and tentative techniques of the American Oil Chemists Society (AOCS).

3.0 RESULTS AND DISCUSSION

The results collected in this study include mass of milled roselle seed sample, mass of roselle seed oil, percentage oil yield, roselle oil properties and roselle methyl esters fuel properties as shown in Tables 1 and 2.

Table 1: Properties of extracted crude roselle oil

Properties	Seed Oil
Free fatty acid %	0.433-2.300
Iodine number (g I2/100 g)	111.4
Saponification value mgKOH/g	125.6
Refractive index (40°C) ms^{-1}	1.4562
Moisture content %	4.0
Peroxide value meq/kg	5.9-9.0
Specific gravity	0.956

3.1 Characterization of the Extracted Crude Roselle Oil

The oil content of the roselle seed obtained in this study was 13.56 %, which was low compared to the yield obtained by [12, 13]. The extracted oil of roselle seeds was subjected to physiochemical analysis using the AOAC (1984) and AOCS (1994) standards methods and the results obtained are shown in Table 1. The oil was yellowish in colour at room temperature with a free fatty acid value which ranged from 0.433-2.300 and refractive index of 1.4562 ms^{-1}. The FFA value obtained in this study was similar to the value reported by [12] and [13]. The Saponification value obtained was comparable to the value reported by [14] but lower than the value reported by [15]. The values obtained for moisture content, iodine number, peroxide value were quite similar to the values reported by [12].

3.2 Roselle Oil Yield

From the results, average oil yield from roselle seed was 13.56 %. The oil yield value obtained in this study was lower than the values obtained by [12] that worked on the impacts of handling roselle seed parameters on its oil output and produced 24.5 percent roselle oil using hydraulic extraction technique. The reduced yield of oil achieved in this research can be ascribed to various variants, genetic, environmental, ecological, oil plant harvesting circumstances, and even the technique of extraction used.

3.3 Roselle Methyl Ester Yield

The transesterification process yielded 52.77 % roselle oil methyl ester on volume basis as shown in Table 2. This output is lower than the 78.80 % obtained by [14] for biofuel production from *Hibiscus Cannabinus* but quite comparable to the value obtained by [16] that reported a yield of 66.81 % for the biofuel produced from melon (*Citrullus colocynthis* L) seed oil methyl ester.

The low yield obtained in this study can be attributed to the difference in several process parameters such as: alcohol / oil molar ratio, catalyst used, temperature and time of reaction, moisture existence and free fatty acids (FFA).

3.4 Characterization of the Biofuel

The characterization of the biofuel produced was carried out. Some of the results are presented in Table 3 with their respective threshold set for biodiesel fuel standard (ASTM D6751) .

Table 2: Roselle oil Methyl Ester yield

Experimental runs	Volume of roselle oil/mL	Volume of roselle oil methyl ester/mL	Ester yield, %
1	40	20.20	50.50
2	45	24.15	53.67
3	50	27.07	54.14
Average			52.77

Table 3: Some properties of roselle biofuel against ASTM D6751 biodiesel standard

Property	Limit (ASTM D6751)	Roselle Oil Methyl Ester
Kinematic viscosity at 40^{0}C (mm^2/s)	1.9–6.0	4.56
Density at 15°C (g/cm^3)	0.860-0. 900	0.874
Cloud point (°C)	Nd	4
Cetane number	55	54

Property	Limit (ASTM D6751)	Roselle Oil Methyl Ester
Flash point (ºC)	>130	206
Pour point (ºC)	Nd	-3
Fire point (ºC)	Nd	210
Acid Value (MgKOH/g)	<0.80	0.42
Iodine Value (g I_2/100 g)	Nd	0.62
Saponification Value (MgKOH/g)	Nd	0.16
Specific Gravity at 29ºC	<0.9	0.895

Source: Standard values of Biodiesel were extracted from the ASTM D6751; **Nd =**Not defined.

From the results obtained in Table 3, the Cetane number of the roselle methyl ester was 54 which is in agreement with the values reported by [17] and [19]. The flash point and fire point of the biofuel produced were 206 °C and 210 °C respectively. A higher flash point than the one reported by [17] was obtained in this study however, it is in agreement with the ASTM D6751 biofuel standard.

The pour point and cloud point obtained for roselle biofuel were -3 ºC and 4 ºC respectively. The low value recorded for the pour point agreed with the values reported by [17-19]. This value indicated a limit to the use of the roselle biofuel in low-temperature conditions according to [20]. This challenge can however be adjusted by proper blending with the Conventional diesel [3]. The cloud point had no specified international standards but a higher value than the one reported by [17] was recorded. The density, kinematic viscosity and specific gravity for the roselle biofuel were in agreement with the trends reported in [21], [19] and [17] The acid value of 0.42 MgKOH/g was recorded which is in accordance with the ASTM D6751 standard. Acid value is a parameter characterizing the degree of fuel ageing during storage as it gradually rises owing to biodiesel degradation [22]. The iodine number for roselle methyl ester was 0.62 gI_2/100g. This indicates the chemical stability properties of the biofuel against oxidation. The greater the iodine value, the greater the double bond number and therefore the lower its stability [23].

4.0 CONCLUSIONS

As shown in this research, roselle seeds as agricultural by-products of the roselle processing industry could be channeled into sustainable use as demonstrated. This research shows that in the presence of a heterogeneous catalyst (ZnO and CaO), biodiesel can be effectively produced from crude roselle seed oil through transesterification with methanol. Some of the properties of the roselle methyl ester investigated in this study showed better results which did not deviate from the ASTM D6751 standard. It may therefore be concluded that the biofuel produced from crude roselle oil is a prospective fossil diesel substitute.

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