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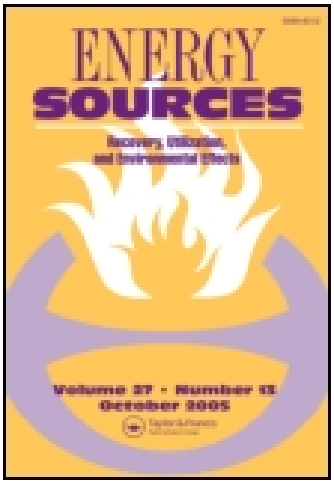

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A process for the production of the ethyl ester from "used frying oil" for use as biodiesel fuel has been studied. The essential part of the process is the transesterification of the used frying oil with ethanol, in the presence of a catalyst (NaOH), to yield the ethyl ester as a product and glycerine as a by-product. Prior to the use of the waste vegetable oil as a feedstock in the production of biodiesel, the oil sample was treated with silica gel as an adsorbent and the results obtained indicate that the treatment method employed positively affects the free fatty acids and iodine value of the oil. Results obtained on the characterization of the biodiesel produced also shows that the viscosity, density, flash point, pour point, sulphur content, vapor pressure, and heat of combustion are 4.8 cP, 850 g/cm^3, 145°C, −15°C, 0.02%, 64 kPa, and 42,600 kJ/kg, respectively. These values compared favorably with the petro diesel. The distillation properties of the produced biodiesel also compared favorably with that of the petro diesel with an initial boiling point of 141°C, final boiling point of 347°C, total recovery of 97.74%, with residue and loss of 1.23 and 1.03%, respectively.

Keywords: biodiesel, petro diesel and energy, qualities of biodiesel, waste vegetable oil

1. INTRODUCTION

Across the globe, environmental concerns and energy security issues have prompted legislation and regulatory actions spurring demand for alternative fuels, and biodiesel has been considered as a perfect alternative source of energy (Abdulkareem et al., 2010). However, the greatest driving force for the use of biodiesel and biodiesel blends is the necessity to have a fuel that fulfills all of the environmental and energy security needs that do not sacrifice operating performance (Zhang et al., 2003a; Wang et al., 2007). Biodiesel is not a new technology; it was introduced in South Africa before World War II to power heavy duty vehicles. The discovery of fossil fuel as a cheap, safe, and efficient source of energy discouraged the usage of biodiesel. Recent environmental and

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domestic economic concerns have prompted a resurgence in the use of biodiesel throughout the world (Abdulkareem et al., 2010).

Biodiesel can be produced through transesterification, a process that combines vegetables oils, animal fats, and/or micro algae oils with alcohol in the presence of a catalyst to form a fatty ester (Zhang et al., 2003b; Attanotho et al., 2004; Helwani et al., 2009; Freedman et al., 1986; Darnoko and Cheryan, 2000). The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials that resulted in a food versus fuel dispute (Aghan, 2005). The concerns that biodiesel feedstock may compete with the food supply in the long term has resulted in searching for alternative methods from vegetable oils. Efforts are now direct towards the use of nonedible, industrial oil, or waste vegetable oil for biodiesels production (Refaat, 2010; Hossain and Boyce, 2009; Morais et al., 2010; Chhetri et al., 2008). The term "waste vegetable oil" refers to vegetable oil that has been used in food production and is no longer viable for its intended use. Waste vegetable oil arises from many different sources, including domestic, commercial, and industrial. It is a potentially problematic waste stream, which requires to be properly managed and its disposal can be problematic when disposed incorrectly down the kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies (Refaat, 2010). Properties of degraded used frying oil after it gets into a sewage system are conductive to corrosion of the metal and concrete elements. It also affects installation in wastewater treatment plants, which adds to the cost of treating effluent or pollutes the waterways. The economic and environmental impact of waste vegetable oils favored its choice as the feedstock for the production of biodiesel, which is the focus of this study. Biodiesel from used frying oil leads to a far better life cycle analysis (Refaat, 2010). It has to be realized that the effect of CO_2 saving is significantly higher when using used frying oil as feedstock, because the effects of the agricultural production of vegetable oils is not taken into consideration (Helwani et al., 2009). The literature also reveals that waste vegetable oil biodiesel showed a net energy ratio (NER) of 5–6 compared to 2–3 for rapeseed or soybean biodiesel and 0.8 for petro diesel (Refaat, 2010; Bernard et al., 2007). The NER is evaluated by dividing the energy output of the system by the cumulative energy demand of the system. Furthermore, the processing of used frying oil into biodiesel is an ideal alternative to the use as animal feed, which is restricted by the law in Europe. The product, therefore, has the other benefits of being removed from the food chain. The limiting factor is the limited availability of used cooking oil on the market. Oil collection from household, commercial, or industrial sources can be achieved through grease traps or through a holistic policy framework, and process industries are adopting more energy-efficient technologies to improve its profitability and competitiveness (Refaat, 2010).

2. EXPERIMENTAL

The process of producing biodiesel from waste vegetable oil involves collection and pretreatment of the used oil. This was then followed by the transesterification process. At the end of the reaction, the products were separated into two layers; the ester product formed the upper layer and the by-product glycerine formed the lower layer. The residual catalyst and unreacted excess alcohol were distributed between the two phases. After separation of the phases, the catalyst and alcohol were washed from the ester with water. Below are the detailed procedures of the experimental analysis conducted in this study.

2.1. Collection and Preparation of Used Frying Oil

The raw material (used frying oil) was collected from Lace restaurants in Tunga, Minna, Niger-State, Nigeria. The used cooking oil was filtered to remove food residues and solid precipitate in

the oil. Hence, the filtered used frying oil was subjected to drying by heating at 60°C for 10 min using a microwave oven.

2.2. Pretreatment of the Used Frying Oil

A known volume (300 cm^3) of the oil was dissolved in 100 cm^3 of *n*-hexane; the mixture was then mixed with silica gel in a ratio of 1:1. The mixture of oil and hexane with the adsorbent (silica gel) was stirred vigorously for 30 min using a Gallen Kamp orbital shaker, after which it was transferred into a round-bottom flask and kept in an incubator for vacuum filtration to remove the solvent and water present. The pretreated oil was analyzed for free fatty acid and peroxide value (PV). All of the experimental analyses were conducted in triplicate and the results presented are the average values. The chemicals used in this work were also of analytical grade (98–99.9%).

2.2.1. Determination of Free Fatty Acid in Used Frying Oil (Acid Value)

A known weight (1 g) of the oil was poured into a conical flask and 50 cm^3 of alcohol was added followed by the addition of three drops of phenolphthalein and then shaken vigorously. The mixture was then titrated with 0.5 M of sodium hydroxide (NaOH) solution with constant shaking until the color changed to pink. The percentage of free fatty acid in the samples was then calculated using the relationship shown in Eq. (1):

$$\text{Free fatty acid } (\%) = \frac{\text{Titer value} \times 0.14}{\text{Weight of sample}} \times 100. \tag{1}$$

2.2.2. Determination of Peroxide Value

One gram of the oil sample was weighed and added to 1 g of potassium iodide. This was then followed by the addition of 20 cm^3 of glacial acetic acid and chloroform in a ratio of 2:1 and boiled for 1 min. The mixture was transferred into a flask containing 20 cm^3 of 5% potassium iodide solution. Three drops of starch solution were added and titrated with 0.025N $Na_2S_2O_3$ to a faint yellow color, followed by the addition of 1 cm^3 of starch indicator, and continued with titration until the blue color disappeared. The peroxide value was calculated using Eq. (2):

$$\text{Peroxide value } (\%) = \frac{\text{Titer value} \times N}{\text{Weight of sample}} \times 100. \tag{2}$$

2.3. Preparation of Ethyl Ester

The transesterification experiment was performed using 100 cm^3 of the pretreated used frying oil and 160 cm^3 of ethanol, which represented a 100% excess of the stoichiometrical amount required for the transesterification. The required amount of the catalyst (3.5 g) of sodium hydroxide was quickly weighed in a closed weighing machine and dried in a microwave oven for 1 min. The dried catalyst was added to the ethanol and was vigorously stirred with a gentle heating until it completely dissolved in the ethanol. The ethanol and the dissolved catalyst were then added to the oil and were stirred vigorously. The mixture was heated at 60°C using a microwave oven equipped with a magnetic stirrer and non-contact infrared continuous feedback temperature system, which allowed continuous vigorous stirring and constant temperature control. The reaction mixture was irradiated using 50% of an exit power of 750 W for 5 min. An additional 15 cm^3 of water was added to the reaction mixture. After allowing it to stand at room temperature for 5 min, the reaction

mixture was poured into a separator funnel; the top ester (biodiesel) layer was poured into another flask and transesterified three times for proper phase separation and maximum conversion.

2.3.1. Washing and Analysis of the Biodiesel

First, 100 cm^3 ethyl ester (biodiesel) was separated and excess alcohol and residual catalyst were washed from the ethyl ester with 20 cm^3 of water by placing the ethyl ester in a glass cylinder and spraying with water at low velocity. The excess alcohol and catalyst were removed by the water as it percolated through the cylinder. Microwave heating at 60°C for 3–4 min was again used to speed up the separation process. After the heating, the cylinder was left to stand at room temperature for 10 min, after which the water phase containing the unreacted alcohol and catalyst would settle, leaving a clear ethyl ester (biodiesel) on top. The produced biodiesel was then analyzed to determine the density, sulphur content, viscosity, pour point, flash point, and distillation characteristics (Abdulkareem et al., 2010; Adeniyi et al., 2007).

3. RESULTS AND DISCUSSION

Biodiesel is a renewable diesel fuel or bio fuel that can be produced by combining any natural oil or fat with methanol or ethanol by chemical means. Oil or fat sources that are locally available can be used as feedstock and it is now adopted by many nations as an alternative source of energy. Presently, several countries, such as Brazil, United States, Germany, Australia, Italy, and Austria, are already using bioethanol or blended diesel and biodiesel (Refaat, 2009). Other countries, such as Malaysia, use blended fuel (5% palm oil and 95% regular diesel). It is expected that this trend will grow and more countries will use bio fuels as a complementary strategy for sustainability (Helwani et al., 2009). Despite the huge interest in biodiesel, its adoption in developing countries like Nigeria has been limited and much lower than the United States and most other European countries. For most Nigerian individuals and companies, the production and sale of a biodiesel is a new venture. The objective of this study, therefore, is to produce a biodiesel from the used frying oil as an alternative to petro diesel with the aim of reducing the over dependency of petro diesel, scarcity of diesel fuel, and environmental impact of petro diesel. Various analyses, such as sulphur content, density, flash point, pour point, viscosity, vapor pressure, calorific value (heat of combustion), and distillation properties were conducted and the results obtained are presented.

Table 1 presents the effects of treatment of the used oil with silica gel as the adsorbent on the free fatty acids and iodine value. Free fatty acid is one of the important parameters used in measuring the quality of palm oil. It indicates the level of rancidity that is taking place in the oil. Presence of free fatty acids in a significant amount in the oil used as a feedstock in a biodiesel production has an effect on the quality and quantity of biodiesel produced (Turapan et al., 2010). For instance, in the production of biodiesel from the used vegetable oil with sodium hydroxide as the catalyst, excessive presence of free fatty acid will react with the catalyst to produce soap. The soap produced affects the separation of biodiesel from glycerol. The presence of free fatty

TABLE 1
Properties of the Used Frying Oil with Silica Gel as an Absorbent

Sample	*Titer Value*	*Free Fatty Acid (FFA), %*	*Peroxide Value (PV), %*
Used frying oil before pretreatment	3.20	8.96	6.70
Used frying oil after pretreatment	2.19	6.17	3.50

acids above the required amount in the oil for the production of bio diesel also affects the cost of production because more catalyst will be required by the reaction. Therefore, it is important to treat the oil before using it in the production of biodiesel. As observed from Table 1, the percentage of free fatty acid of the pretreated oil was found to be 6.17% for a titer value of 2.19. Similarly, the percentage free fatty acid (%FFA) of the untreated oil was found to be 8.96% for a titer value of 3.20. Although it has been reported that fresh oil should contain a maximum of 5% free fatty acids for nutritional purposes (Ugwu et al., 2002), the results reported indicate that the values of free fatty acids in both the treated and untreated oil is higher than the required limit. However, it can be inferred from these results that the treatment method adopted in this work was able to reduce the percentage of free fatty acids in the oil. Also presented in Table 1 are the effects of treatment on the iodine values of the oil sample. Iodine value is used to measure the level of unsaturation in the oil. It has been reported that high value of iodine in the oil is an indication that the oil sample is highly unsaturated and it can be easily oxidized. Therefore, addition of antioxidants is important to improve the qualities of the oil, which will also affect the cost of production and qualities of the biodiesel produced from such oil. As observed from Table 1, the peroxide value of the pretreated oil was 3.5%, for a titer value of 2.19. Similarly, the peroxide value of the untreated fried oil was 6.7% for a titer value of 3.20; these values are much lower than the peroxide value of the fresh oil, which is 53%.

To achieve proper conversion of the used vegetable oil to biodiesel, the oil and alcohol were properly mixed with excess alcohol (Agarwal and Das, 2001). Results obtained on the properties of biodiesel produced are shown in Table 2. As observed in Table 2, the flash point of the produced biodiesel was 145°C compared to petro diesel, which is 65°C. Flash point is described as the lowest temperature at which the produced biodiesel can vaporize to form ignitable mixture in the air. Results obtained as presented showed that the flash point of ethyl ester produced biodiesel was higher than that of petro diesel. The higher value of the flash point of the produced biodiesel compared to the petro diesel is an indication that the produced biodiesel contains highly flammable and volatile materials; therefore, care must be taken when using the biodiesel. Also presented in Table 2 is the viscosity of the biodiesel produced. The viscosity of oil is an important parameter used to determine the qualities of oil with reference to the flow of oil in the pipelines, injection nozzle, and orifices (Abdulkareem et al., 2010). Results obtained indicated that the viscosity of the biodiesel at 40°C is 4.8 cP, which is higher than that of the petro diesel, which is 3.2 cP at

TABLE 2
Properties of Biodiesel from Used Vegetable Oil

Properties	*Ethyl Ester (Biodiesel)*	*Petrol Diesel*
Viscosity at 40°C (cP)	4.8	3.2
Density (g/cm^3)	850	820
Flash point (°C)	145	65
Pour point (°C)	−15	−10
Sulphur content (%)	0.02	0.05
Vapor pressure (kPa)	6.4	0.2
Calorific value (heat of combustion) (kJ/kg)	42,600	44,800
Distillation properties		
IBP (°C)	141	
FBP (°C)	347	385
Total recovery (%)	97.74	90
Residue (%)	1.23	
Loss (%)	1.03	

the same temperature. The rapid vapor pressure of the biodiesel is 6.4 kPa; this is higher than that of the petro diesel, which is 0.2 kPa. Vapor pressure is used to measure the volatility of oil. It determines how easily a liquid vaporizes or changes into a gas. Though oil is supplied in liquid form, it is necessary that a small part of it must be vapor to ignite in an engine combustion chamber. Therefore, little volatility could result in failure of the car to start and excess volatility could result in vapor lock, when combustion fails to occur because the liquid fails to change to gaseous fuel in the fuel chamber rendering the fuel pump to be ineffective. It can be inferred from these results that the produced biodiesel can be used easily without much modification in hot and cold weather. The density of the ethyl ester (biodiesel) produced at a corrected temperature of 15°C was 850 g/cm^3 compared to a standard diesel fuel, which is 820 g/cm^3. It was observed that the ethyl ester (biodiesel) has a higher density, which means that the ethyl ester (biodiesel) is denser than the diesel fuel; the pour point of the ethyl ester (biodiesel) was −15°C and this was the temperature at which the movement of the oil will be observed when cooled. The pour point of petro diesel fuel is −10°C compared to the value obtained of ethyl ester (biodiesel), which showed that the petro diesel fuel was higher than that of the produced biodiesel. Other analyses conducted on the biodiesel, as shown in Table 2, are the sulphur content and heat of combustion, also known as the calorific value. Calorific value is a measure of the quantity of heat produced by the combustion of oil at constant pressure. It also shows how the water produced as a result of combustion of oil is condensed and how the heat contained in the water vapor is recovered. Results obtained reveal that the heat of combustion of the biodiesel produced from the used vegetable oil is 42,600 kJ/kg; this value is close to that of the petro diesel, which is 44,800 kJ/kg. Results obtained on the characterization of the biodiesel also indicated that the sulphur content of the biodiesel is 0.02%, which is much lower than that of the petro diesel at 0.05%.

The distillation characteristic of the produced biodiesel is presented in Table 3, and the results obtained show that the distillation recovery of the biodiesel produced was 97.74%. The percentage residue was 1.23 and the percentage loss was 1.03 of the quantity distilled, the range of loss for petro diesel is between 0.1 and 1.0, and the value obtained from the produced biodiesel falls within the range, which showed that the product would give a greater efficiency.

TABLE 3
Distillation Characteristics Obtained

Percentage Recovery, cm^3	*Temperature (°C) Value Sample = 100 cm^3*
IBP[a]	141
10%	255
20%	261
30%	272
40%	280
50%	290
60%	297
70%	312
80%	321
90%	335
FBP[a]	347
Total recovery (%)	97.74
Residue (%)	1.23
Loss (%)	1.03

[a]IBP: initial boiling point; FBP: final boiling point.

4. CONCLUSIONS

Based on the results of analyses conducted on the biodiesel produced from used vegetable oil, it can be deduced that the production of biodiesel from used frying vegetable oil is feasible, after treatment of the used oil is also important if the used vegetable oil is to be considered as a feedstock in the production of biodiesel. Characterization of the biodiesel produced also shows that properties, such as viscosity, density, heat of combustion, pour point, and sulphur content, compared favorably with the petro diesel, while the vapor pressure and flash points of the produced biodiesel are higher than that of the petro diesel.

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