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# RICE BRAN OIL BIODIESEL

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## A B S T R A C T

The search for cheap alternative sources of vegetable oil, the need to convert agricultural wastes to wealth and the desire to solve waste disposal problems has lead to the extraction of oil from rice bran. The oil was extracted using a soxhlet extractor operated at 60$^oC$ and then transesterified using methanol as reagent and sodium hydroxide as catalyst. No pretreatment with an acid was necessary as the free fatty acid was a low 0.12%. The oil and biodiesel were characterized according to American Society for Test and Materials (ASTM) and the European Norms (EN) protocols. The results obtained shows that the densities and viscosities of the oil reduced after transesterification, while flash points and cetane number of the samples increased. Most of the properties are within the limits of ASTM D6751-02 standards for biodiesel thus making it a suitable alternative fuel for diesel engines.

**Keywords:** Rice bran oil, transesterification, biodiesel, characterization.

## INTRODUCTION

The use of vegetable oil and animal fats for the production of biodiesel has been strongly criticized because of the possible adverse effects on food security if land used for food production is diverted to the production of vegetable oils for biodiesel or if oil for consumption is used for biodiesel production. This concern has led to research in the use of non-edible oils such as castor oil (Bello and Otu, 2011) and rubber seed oil (Ramadhas et al, 2009) as feedstocks for the production of biodiesel. Jatropha for example, which is inedible, can be used as hedge crop, can be planted on local dump sites, marginal and semi-arid lands, and do not require chemical inputs and maintenance. However, if oil from waste products such as used frying oil (Lague et al.,1987) or fish wastes (Cherng-Yuan and Rong-Jilia, 2008) are used, they would also solve disposal problems and help to create wealth from apparently valueless and disgusting farm or factory wastes. Rice bran falls into this category of factory wastes that for ages have been burnt to dispose off and without any economic value notwithstanding the fact that it contains triglycerides.

## LITERATURE REVIEW

Rice (*oryza sativa linn*) bran is the outer brown thin layer between the rice and the outer husk of the paddy that is removed in order to polish the rice and constitutes approximately 8% of the gross weight of a harvested rice head. The whole rice grain comprises (on dry weight basis): Endosperm 70-72%, Hull 20%, Bran 7.0-8.5% and Embryo 2-3% while the rice bran comprises pericarp, tegmen (layer covering endosperm), aleurone and sub – aleurone (Ju and vali, 2005). Depending on the specie and intensity of milling, the oil content of rice bran has been reported to be 16 – 32 wt% (Hargrove, 1993), which is much lower than the 55% for jatropha (Pramanik, 2003), 55% for castor (Conceicao et al., 2007) and 60% for egunsi seeds oil (Giwa et al., 2010) and 45% for rubber seed oil (Ramadhas et al., 2009).

When rice is used as feedstock for the production of oil instead of being regarded a waste, it would have more positive impact on food supplies than when edible crops like Soya beans and corn are used because it is a by-product and does not require extra land, labour and other farm inputs for its planting.

Due to the presence of an active lipase in the bran, Free Fatty Acid (FFA) content in Rice Bran Oil (RBO) has been reported to be much higher than other edible oils and about 60-70% of the oil produced from this bran is non-edible, due to problems attributable to the stability and storage of rice bran and the dispersed nature of rice milling (Goffman, 2003; Zullaikah et al., 2005; Lin et al., 2009). The FFA of the oil usually increase rapidly to 4 - 8%, due to the active lipase in the bran after milling and constitutes a major hurdle during transesterification and the dark color during refining (Bhattacharyya, 1983).

RBO has been classified as one of the most nutritious oils due to its favorable fatty acid composition and a unique combination of naturally occurring biologically active and antioxidant compounds (Goffman, 2003). the edible part is commonly used as cooking oil in china, Japan and India, and the bran is used as a fiber component for poultry and cattle feeds in the United States.

A survey of the use of rice bran in rice mills in Nigeria shows that it is used as furnace fuel for drying, fish and cattle feeds and in the majority cases it constitutes a waste. Whereas in countries such as India and Thailand where rice is widely cultivated, it has been researched extensively (Yi-Hsu J. and Shaik Ramjan V., 2005; Venkanna et al., 2009; Syed Altaf et al.,2009) and reported.

The aim of this study is to extract oil from the rice bran and characterize the oil and its biodiesel.

## MATERIALS AND METHODS

Rice bran was obtained from rice mills located in Ikogosi in Ekiti states of Nigeria. The powdery form of bran was procured immediately after milling and stabilized into flakes and dried as it has been reported that it allows for 96% oil extraction within 5 minutes and after 1 hour the residual oil was about 0.7% (dry weight basis) (Bender, 1999). The oil was extracted in a soxhlet extractor using *n*-hexane as the solvent. The oil was leached for 8 hours with the mantle heater set at $60^{o}$ C and the residual hexane in the mixture was removed using a vacuum rotary evaporator operated at $75^{o}$ C.

The oil obtained was weighed and the percentage oil yield was calculated by the equation 1.

$$\text{Oil yield } \% = \frac{\text{Weight of oil extracted}}{\text{Weight of rice bran used}} \text{x}100 \qquad 1.$$

The Free Fatty Acids (% oleic acid) content of the oil were first measured to determine if pretreatment was necessary or not before alkaline transesterification as it has been reported that too high acid content during alkaline transesterification can react with the catalyst to form soap which can inhibit biodiesel yield (Ramadhas et al., 2009). This was found to be 0.12%, which was lower than the minimum of 3% often reported (Ramadhas et al., 2009; Sahoo et al., 2007) hence no pretreatment was done.

**Transesterification Procedure**

Transesterification was carried out using a laboratory scale biodiesel processor in the Fuel Laboratory of the Federal University of Technology, Akure. The optimum reaction conditions for the transesterification of rice bran oil using the orthogonal analysis of parameters in a four-factor and three-level test, obtained by Ju and Vali (2005) were used. The alkaline transesterification was done using anhydrous methanol at a molar ratio of 6 to 1 and 0.9 % w/w of sodium hydroxide. The processor was stirred at 600 rpm and at a temperature of 60 $^{o}$C for 4 hours after which the mixture was poured into a decanter and allowed to settle for 3 hours so that the reaction can be driven to completion and for the mixture to separate into methyl ester and for the glycerol at the bottom to be drained off by gravity. The excess methanol in the ester was removed in a flash evaporator. To remove any impurity, the methyl ester was washed in distilled water of volume ratio 3 to 1 three times. The biodiesel yield was calculated from the biodiesel and oil weights using equation 2:

$$\text{Yield}\ \% = \frac{\text{Weight of oil used in reaction}}{\text{Weight of biodiesel produced}}\ \text{X}100\% \qquad 2.$$

**Fatty Acid Profile**

The fatty acid profile of rice bran oil (RBO), the B100 and the standard sample of free fatty acid were determined using the HP 6890 Gas Chromatography analyzer that used HP ChemStation Rev A 09.11 [1206] software for data collection. It was equipped with a Flame Ionization Detector (FID) and used nitrogen as the carrier gas. The initial oven temperature was set at 60 $^{o}$C and the procedure was as reported by (Bello and Otu, 2011).

**Characterization**

The rice bran oil and its methyl ester (B100), where characterized according to ASTM and EN protocols as listed in Table 1. Measurements were made in triplicate and the mean reported.

**Table 1. Biodiesel properties test methods**

| Property | Unit | Protocol | ASTM Limits D6751 | EN Limits 14214 |
|---|---|---|---|---|
| **Density at 15$^{o}$C** | kg/m$^{2}$ | ASTM D1298 | 860-900 | 860-900 |
| **Pour point** | $^{o}$C | ASTM 2500 | - | - |
| **Cloud point** | $^{o}$C | ASTM2500 | - | - |
| **Flash point** | $^{o}$C | ASTM D93 | 130 min | 120 min |
| **Kinematic viscosity** | mm$^{2}$/s at 40 $^{o}$C | ASTM D445 | 1.9-6.0 | 3.5-5.0 |
| **Lower heating value** | kJ/kg | ASTM D240 | - | - |
| **Cetane index** | - | ASTM D613 | 47 min | - |
| **Iodine value** | g/100g | EN14111 | 120 | - |
| **Peroxide value** | meq/kg | EN14111 | - | - |
| **Oxidation index** | hours | ASTM D2709 | 3 min | 6 min |
| **Saponification value** | mg KOH/g of oil | EN14111 | - | 120 max |
| **Free fatty acid** | % oleic acid | - | - | - |

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|---|---|---|---|---|
| **Acid value** | mgKOH/g | ASTM D664 | 0.05max | - |
| **Soap content** | Ppm | EN14111 | - | - |
| **Water and residue** | % | ASTM D2709 | 0.05 max | - |
| **Moisture content** | % | ASTM D2709 | - | 360 max |
| **Sulphur** | % | ASTMD5453 | 0.05% | |
| **Copper strip Corrosion** | | ASTMD130 | No.3 max | |

## RESULTS AND DISCUSSION

The fatty acid profile of the oil and B100 are shown in Table 1 while the characterization results are in Table 2. The percentage free fatty acid value was surprisingly very low, thus making pretreatment with an acid unnecessary [Ramadhas, 2009]. The oil yield was 15%, which is comparable to the 13 - 23 % reported by Houston (1972) and it had a brownish green colour with very pungent smell.

### Fatty Acid Profile

**Table 2. Fatty Acid Profile of Rice Bran Oil (RBO) and B100.**

| Acid | Form | RBO | B100 |
|---|---|---|---|
| **Myristic** | C14:0 | 0.112 | 0.078 |
| **Palmitic** | C16:0 | 14.991 | 15.926 |
| **Palmitoleic** | C16:1 | 0.146 | 0.1009 |
| **Margaric** | C17:0 | 0.028 | 0.019 |
| **Stearic** | C18.0 | 1.288 | 1.275 |
| **Oleic** | C18:1 | 41.513 | 40.914 |
| **Linoleic** | C18:2 | 38.652 | 38.474 |
| **Linolenic** | C18:3 | 1.416 | 1.429 |
| **Arachidic** | C20:0 | 0.765 | 0.778 |
| **Arachindonic** | C20:4 | 0.243 | 0.168 |
| **Behenic** | C22:2 | 0.588 | 0.615 |
| **Erucic** | C22:1 | 0.034 | 0.023 |
| **Lignoceric** | C24:0 | 0.222 | 0.199 |
| **Total Saturation** | | 17.406 | 18.275 |
| **Total unsaturation** | | 82,592 | 81.929 |

**Table 2. Fatty Acid Profile of different Rice Bran Oil17.406 biodiesel**

| Acid | Form | RBO | Nigeria B100 | *B100 | **B100 |
|---|---|---|---|---|---|
| **Lauric** | C12:0 | - | - | - | 0.2 |
| **Myristic** | C14:0 | 0.112 | .078 | 0.40 | 0.8 |
| **Palmitic** | C16:0 | 14.991 | 15.926 | 15.60 | 17.7 |
| **Palmitoleic** | C16:1 | 0.146 | 0.1009 | - | 0.23 |
| **Margaric** | C17:0 | 0.028 | 0.019 | - | - |
| **Stearic** | C18.0 | 1.288 | 1.275 | 2.00 | 2.2 |
| **Oleic** | C18:1 | 41.513 | 40.914 | 41.00 | 40.6 |
| **Linoleic** | C18:2 | 38.652 | 38.474 | 33.5 | 35.6 |
| **Linolenic** | C18:3 | 1.416 | 1.429 | 0.50 | 1.8 |

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|---|---|---|---|---|---|
| **Arachidic** | C20:0 | 0.765 | 0.778 | 0.2 | 0.2 |
| **Arachindonic** | C20:4 | 0.243 | 0.168 | | - |
| **Behenic** | C22:2 | 0.588 | 0.615 | - | 0.3 |
| **Erucic** | C22:1 | 0.034 | 0.023 | - | - |
| **Lignoceric** | C24:0 | 0.222 | 0.199 | - | 0.6 |

*Zullaihikah et al., 2005 **Houston, 1972

**Biodiesel Analysis**

The main components of the fatty acid profile of the RBO and B100 were analyzed qualitatively and quantitatively using GC-MS and GC-FID and the results are shown in Table.2. The oil contains 14.991% palmitic and 1.288% stearic acids both of which are saturated, and 41.513% oleic, 38.652% linoleic and 1.416% linolenic acids. The profile for the methyl ester followed the same pattern, but the mass of the fatty acids with double and triple bonds in B100 decreased while that of the monounsaturated fatty acid increased. Of particular significance is the oleic acid of 41.513% for the oil which is just below the average value of 45% for vegetable oils [Bello and Agge, 2011]. Oleic acid value gives the balance between favorable cold flow properties, high oxidation stability and tendency for soap formation during transesterification. However, The fatty acid profile does not meet the quality specification of Schenk et al. 2008, that suggested that a good quality biodiesel should have a 5:4:1 mass fatty acid ratio of C16:1, C18:1 and C14:0, but it agrees with the chemical structure of biodiesel proposed by Li et al., (2005) in the form $C_{19}H_{36}O_2$. Since C18 fatty acid methyl ester constituted 82.869 % of the biodiesel. The results obtained in this study are comparable to those reported by Zullaihikah et al., 2005 and Houston, 1972 as shown in Table 2.

**Table 3. Properties of bran oil, its biodiesel and blends.**

| Property | RBO | B100 |
|---|---|---|
| **Density (kg/m$^{2)}$** | 906 | 885 |
| **Pour point ($^{o}$C)** | 13 | 2.5 |
| **Cloud point($^{o}$C)** | 16 | 3.3 |
| **Kinematic viscosity (mm$^2$/s at 40 $^{o}$C)** | 38.2 | 4.54 |
| **Flash point ($^{o}$C)** | 184.0 | 162.8 |
| **Lower heating value (kJ/kg)** | 40.85 | 41.60 |
| **Cetane index** | 51.02 | 56.95 |
| **Iodine value (g/100g)** | 103.17 | 112.15 |
| **Peroxide value (meq/kg)** | 1.02 | 1.24 |
| **Oxidation index (Hrs)** | 16 | 9 |
| **Saponification value (mg KOH/g of oil)** | 186.51 | 204.24 |
| **Free fatty acid (% oleic acid)** | 0.12 | 0.14 |
| **Acid value (mgKOH/g)** | 0.06 | 0.08 |
| **Soap content (ppm)** | 0.002 | 10.20 |
| **Water and residue (%)** | 2.00 | 0.005 |
| **Moisture content (%)** | 0.020 | 0.010 |
| **Sulphur** | 0.25 | 0.009 |
| **Copper strip Corrosion** | 4 | 2 |
| **pH value** | 5.76 | 6.92 |

| | | |
|---|---|---|
| **Reflective index** | 1.48 | 1.353 |
| **Colour** | Brownish green | Dark brown |
| **Odour** | Pungent | |

**Density**

This is the mass per unit volume and hence affects the fuel mass flow rate into the engine and the power output from the engine. It affects the pressure of the fuel being injected into the engine and the resulting penetration distance of the injected fuel, the atomization and the combustion process. The density of the oil of 906 $kg/m^3$ reduced to 885 $kg/m^3$ for the B100. Low density has been reported to require advancing the injection timing (Gamus, 2010) to enhance the engine operation.

**Cloud point**

The cloud point is the temperature at which wax would first appear on the surface of the fuel when being cooled. This test is of importance because the presence of wax can affect fuel flow, volatility, uniformity of property and usability in cold region. The cloud point of the oil was 16 $^oC$ and reduced to 3.3 $^oC$ after transesterification.

**Pour point**

The pour point is the temperature to which the wax in the fuel is enough to turn the fuel to a mass of gel. The pour point reduced from 13 $^oC$ to 2.5 $^oC$. The pour point is much lower than that of diesel fuel thus limiting their used in cold regions without the use of antifreeze additives. Biodiesel with high proportion of saturated fatty acids tends to have high pour point because many saturated fatty acids are solid at room temperature.

**Kinematic viscosity**

The kinematic viscosity is a measure of the resistance of the fuel to flow. It affects the performance of fuel pumps, the atomization of injected fuel, lubricity and the impinging distance upon injection. Biodiesel generally has a higher viscosity than diesel, and thus exhibit inferior atomization and spray characteristic, resulting in a larger mean liquid droplet diameter and a longer ignition delay of the fuel [Hoekman et al., 2012]. When viscosity very high, it makes atomization more difficult, it affects combustion efficiency, lower the performance of fuel pumps and adversely affect exhaust emissions because of incomplete combustion. The kinematic viscosity of the oil was 38.2 $mm^2/s$ and it reduced to 4.52 $mm^2/s$ for B100 and although slightly higher than that of diesel is within the ASTM limits for biodiesel.

**Flash Point**

The flash point of the oil was 184 $^oC$ and reduced to 162$^oC$ for B100. this makes it a much safer fuel in storage and use than diesel. It is about three times higher than that of diesel thus making it a safe fuel from the point of view of safety and fire risk. It will consequently, ignite at a much higher temperature which will result in shorter delay period, better engine performance and reduced exhaust emissions.

## Heating value

This is the amount of heat that can be liberated from a kg of the fuel. The heating value of the oil and B100 are 48.44 kJ/(kg.k) and 41.62 kJ/(kg.k) respectively and consistent with the trend for biodiesel. Heating value affects the engine power output, thermal efficiency, fuel consumption, exhaust emissions, cleanliness of the engine, time between service and vehicle performance.

## Cetane numbers

The cetane number for the raw oil of 51.2 and increased to 56.95 after transesterification. It is a measure of the ignition quality of diesel fuels. It reduces the chemical phase of the ignition delay time for the fuel to seek out the necessary oxygen upon injection into the combustion chamber, it influences ease of starting because of its oxygen content and intensity of the characteristic diesel knock during idling. Biodiesels usually have a higher cetane index than diesel fuel because of its oxygen content and also because some of the fatty acids present in the fuel have very high octane number.

## Free fatty acid

The free fatty acid was 0.12% which is surprisingly very low compared to 3% threshold suggested by (Ramadhas et al., 2009) that would not lead to soap formation that can inhibit biodiesel yield during transesterification.  RBO does not require pretreatment before transesterification because of the low FFA content. This is a great advantage as under industrial condition, pretreatment constitute a significant part of the cost of production.

## Iodine value

The iodine value of the oil of 103.17 (g/100g) increased to 112.15 (g/100g) after transesterification both of which are below the 120 (g/100g) limit for biodiesel. Iodine is a measure of the degree of saturation of a fuel. High unsaturation can lead to the free molecules combining with oxygen to cause the fuel to polymerize or after combustion lead to excessive carbon deposits in the engine combustion chamber.

## Peroxide value

Peroxide values of RBO and B100 of 1.02 and 1.24 meq/kg respectively are moderate and reduced with blending after transesterification. Peroxide value is generally used to determine the degree of rancidity and extent of fuel oxidation  The peroxide values are within the limits for biodiesel.

## Oxidative stability index

The oxidative index of 11 hr for the oil reduced to 9 for B100 but increased with blending. During these periods, the presence of double bonds in the fuel causes reversible reactions in the fuel that can lead to the formation of insoluble sediments and gums that are deposited in fuel tanks and filters, and cause corrosion.

**Saponification value**

The saponification value for the oil was 186.51(mg KOH/g of oil) and less than the average of 200 (mg KOH/g of oil) for vegetable oils. The saponification value of 186 (mg KOH/g of oil) compares with the value obtained by (Muhammad et al., 2008) for the oil. The values are all above the maximum EN limits for biodiesel. A small amount of saponification will help in reducing friction between moving parts in the pump and injectors. But when high can have adverse effect on fuel properties and can also inhibit biodiesel yield during transesterification.

**Acid value**

The acid value and FFA value are surprisingly low compared to other results [Bello and Otu, 2011] and would not require pretreatment with acid. The acid value for the oil was 0.06 mgKOH/g which is very much lower than the 23 mgKOH/g by (Muhammad et al., 2012) High acid value can increase fuel density, change fuel colour, and result in the formation of acidic solution which can lead to increased corrosion and deterioration of fuel properties.

**Soap content**

The soap content of the oil increased after transesterification as a result of the residual soap formed that escaped purification. The soap content of 0.002% for the oil increased to 10.20% for B100 because of the imperfection of the washing process that allows for residual soap. High soap content can cause the fuel to burn irregularly thus decreasing thermal efficiency and opacity, and increasing exhaust emissions.

**Water and residue, and moisture contents**

The water and residue contents reduced from 2% for the oil to 0.005 % after transesterification and washing which is within the limit for biodiesel. Water has high latent heat of evaporation and a small quantity can help in lowering the combustion temperature but excessive can freeze under certain conditions and block the flow of fuel to the engine, can promote microbial growth and accelerate corrosion in fuel systems. The higher density of water can cause adversely affect fuel metering while excessive residue can block filters and nozzles.

**Sulphur content**

The sulphur content reduced from 0.25% to 0.009% after transesterification and reduced further with blending. Sulfur is added to diesel to reduce friction but the amount in diesel has been limited by regulation because the sulfur oxide emitted in the exhaust gas can result in acid rain that can affect vegetation and degrade the environment. It can also damage the catalytic converter elements. Biodiesel spreads when poured on a surface and penetrates pores, cracks and crevices thus making it a very good lubricant. In diesel engine, the fuel lubricates the fuel pump, fuel injection systems and the piston rings. The diesel engine is about 30% efficient with about 20% of the power developed lost to friction and another 7.5% wasted in the engine. The naturally occurring sulfur in RBO which along with the high lubricating properties of biodiesel when used for blending will contribute to reducing friction and hence improved fuel economy, mechanical efficiency and engine durability.

## Copper strip Corrosion

The corrosion value of the copper strip in RBO was 4 out of a scale of maximum value of 5. The value however reduced to 2 after transesterification. This test is important because many components of the fuel system are made from copper alloys and are liable to rust when in contact with RBO.

## Colour

The brownish green colour of the raw oil changed to dark brown after transesterification due to the removal of the colour imparting pigments in the oil after transesterification and purification.

## Refractive index

The refractive index of RBO was 1.48, it decreased to 1.353 after transesterification For the oil the result is similar to that reported by (Muhammad et al., 2012) for the oil. Refractive index is an indicator of impurities in the fuel and the presence of high molecular weight components in the fuel.

## pH values

pH is a measure of the acidity and alkalinity of the oil. The raw oil and biodiesel are acidic.

## CONCLUSIONS

RBO has a low free fatty acid content and can be transesterified without pretreatment with an acid and this will reduce the cost of production when produced on industrial scale. The properties of B100 are close to those of diesel fuel hence it can be used as alternative fuel for diesel engines.

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