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EFFECTS OF BLENDING RICE BRAN OIL BIODIESEL WITH DIESEL ON THE PROPERTIES OF

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Abstract

Some properties of rice bran oil and the biodiesel such as saponification value and iodine value even when within standard limits can be more effective if reduced further. One way of achieving this is to blend with diesel. Rice bran oil was extracted using a soxhlet extractor operated at 60°C. The oil was transesterified directly using methanol and sodium hydroxide without pretreatment with an acid as the free fatty acid content was low at 0.12% oleic acid. The biodiesel produced was used to blend diesel to 10% (B10) and 20% (B20). The oil, biodiesel and blends were characterized using the ASTM protocols and the results obtained shows that the densities and viscosities of the oil reduced after transesterification and blending, while flash points and cetane number of the samples increased. Most of the properties after blending are within the limits of ASTM D6751-02 standards for biodiesel thus allowing them to be used as alternative fuels for diesel engines.

Keywords: Rice bran oil; transesterification; biodiesel; blending; characterization.

Introduction

One of the strongest objections to the production of biodiesel from vegetable oil is competition as food item which can lead to high cost of food and increased cost of production as feedstock can constitute as much as 60 -70 of the cost of raw materials for biodiesel production (Haas et al., 2004). This cost can be considerably reduced if inedible feed stocks such as castor and jatropha, used oils or waste part of edible feed stocks are used for biodiesel production.

Rice (*oryza sativa linn*) bran is the outer brown thin layer between the rice and the outer husk of the paddy that is removed to polish the rice and is approximately 8 percent 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 specie of rice and degree of milling, the bran contains 16 – 32 wt% of oil (Hargrove, 1993) which is much lower than 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). Using rice bran as feedstock for biodiesel production will also help in solving waste disposal problem and would have positive impact on domestic food supplies as the oil is also edible.

Due to the presence of an active lipase in the bran, Free Fatty Acid (FFA) content in Rice Bran Oil (RBO) is 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; Ortheoefer, 1996; Zullaikah et al., 2005). 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 (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; Rogers, 1993). It is commonly used as cooking oil in china, Japan and India, and as a fiber component for poultry and cattle feed in the United States. It has no commercial value in Nigeria and it creates disposal problem in rice mills except when used as feeds in regions where livestock is kept in hedges. Small scale local rice farmers do not polish their rice hence the bran is not removed before being cooked. The tastes are a little bit different and are sweater, starchier, and more nourishing but takes longer to cook than the polished rice imported from say Thailand.

Not all the properties of RBO B100 biodiesel are within the ASTM and EN limits for biodiesel but as reported by Bello (2012) and Alpein and canakci (2009), biodiesel properties can be modified by blending with diesel fuel. The aim of this study is therefore to characterize Nigeria rice bran oil and its biodiesel, and also investigate the effects of blending on the properties of RBO biodiesel.

Blending with conventional diesel fuel with biodiesel is done to reduce demand for diesel fuel, improve engine lubricity, reduce harmful exhaust emissions and increase engine cleanliness (Sahoo et al., 2007). It can also be used to improve the inherently lower heat value of biodiesel and reduce cloud point. Blending thus gives a property balance of the difference between B100 and diesel fuel in terms of performance, emissions benefits and costs.

Materials and Methods

Rice bran was obtained from rice mills located in Ikogosi in Ekiti states of Nigeria. The powdery form of bran was stabilized into flakes and dried. 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 basis) (Bender, 1999). The oil was extracted in a soxhlet extractor with the 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 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; Ghadge and Raheman, 2006) hence no pretreatment was done.

Transesterification and Blending Procedures

Transesterification was carried out using a laboratory scale biodiesel processor in chemistry laboratory of the Federal University of Technology, Akure. The optimum reaction conditions for the transesterification of bran oil obtained by Ju and Vali (2005) using orthogonal analysis of parameters in a four-factor and three-level tests, were used. The material inputs were anhydrous methanol at a molar ratio of 6 to 1 and 0.9% w/w of sodium hydroxide as catalyst. The processor was stirred at 600 rpm, at a temperature of 60 ^{o}C for 60 minutes 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 give enough time for the mixture to separate into biodiesel and glycerol which is at the bottom. And easily drained off by gravity. The excess methanol in the ester was removed in a flash evaporator. To remove any impurity, the biodiesel was washed in distilled water of volume ratio 3 to 1 three times until it became clear. Blending was done at a temperature of 25^{o}C well above the cloud point of both contents and in a stainless steel to prevent degenerating reactions associated with the use of brass, bronze, copper, lead, tin and zinc.

Characterization

The main properties of the oil and its biodiesel were measured using mainly the American Society for Testing and Materials (ASTM) protocols for biodiesel fuels as shown in Table 1. The flash point was determined in a Pensky-Marten closed flash tester (Kehler-model K-16270), cloud point was determined using a high precision cloud point meter while the kinematic viscosity was by glass capillary viscometer. For the heating value, the microprocessor controlled isoperil oxygen bomb calorimeter model 6200 was used. The cetane index was determined by the analyzing fuel samples having a wide variety of ignition qualities. By mixing different kinds of biodiesel and fatty acid methyl ester reagents, a regression analysis of the relationship between the cetane numbers, measured in a constant volume combustion chamber was then obtained and used to determine the cetane number. The peroxide, iodine value, acid and saponification values, and free fatty as oleic acid were determined by EN standard methods. The water and residue level was determined using a centrifuge while the water content was by azeotropic distillation method.

Table 1. Biodiesel properties test methods

Property	**Unit**	**Protocol**	**ASTM Limits D6751**	**EN Limits 14214**
Density at 15°C	kg/m^2	ASTM D1298	860-900	860-900
Pour point	°C	ASTM 2500	-	-
Cloud point	°C	ASTM2500	-	-
Flash point	°C	ASTM D93	130 min	120 min
Kinematic viscosity	mm^2/s at 40 °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	-	-	-
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

Results and Discussion

The physical and chemical properties of the fuel samples are shown in Table 2.

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Table 2. Properties of bran oil, its biodiesel and blends.

Property	RBO	B100	B20	B10
Density (kg/m$^{2)}$	906	885	839	835
Pour point (^{o}C)	13	2.5	2.2	2.3
Cloud point(^{o}C)	16	3.3	3.0	3.20
Flash point (oC)	184.0	162.8	118	122
Kinematic viscosity (mm^2/s at 40 ^{o}C)	38.2	4.54	2.84	2.95
Lower heating value (kJ/kg)	40.85	41.60	45.20	45.80
Cetane index	51.02	56.95	50.13	52.60
Iodine value (g/100g)	103.17	112.15	31.32	21.40
Peroxide value (meq/kg)	1.02	1.24	0.97	0.82
Oxidation index (Hrs)	16	9	23	20
Saponification value (mg KOH/g of oil)	186.51	204.24	176.40	172.10
Free fatty acid (% oleic acid)	0.12	0.14	0.17	0.15
Acid value (mgKOH/g)	0.06	0.08	0.07	0.09
Soap content (ppm)	0.002	10.20	2.04	3.36
Water and residue (%)	2.00	0.005	0.003	0.004
Moisture content(%)	0.020	0.010	0.006	0.008

The properties of B100 are similar to those obtained by Subbaiah et al., (2010) and within ASTM specifications for biodiesel. Detailed discussions of the results are as follows.

Density.

The density of the oil reduced after transesterification from 906 to 885 and reduced further with increasing percentage of diesel in the blends as shown in Figure 1. High density will increase the mass of fuel injected, increase energy per unit volume of the fuel but can result in non stoichiometric air/fuel ratio and hence incomplete combustion with consequential increase in pollution and reduction in thermal efficiency.

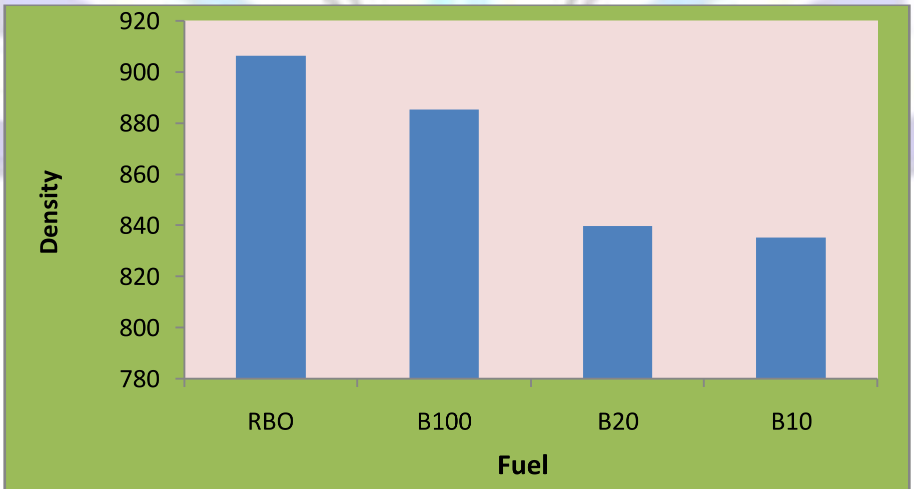

Fig. 1 Variation of density

Cold Flow Properties.

The cold flow properties are shown in Figures 2. The high pour and cloud points of the oil are consistent with its high viscosity. There is not much difference between the pour and cloud points for B100, B10 and B20. The values are however, above those for diesel which would limit their applications in cold regions where there can be subzero temperature. Cold flow properties are important for engine starting and continuing operation at low temperature.

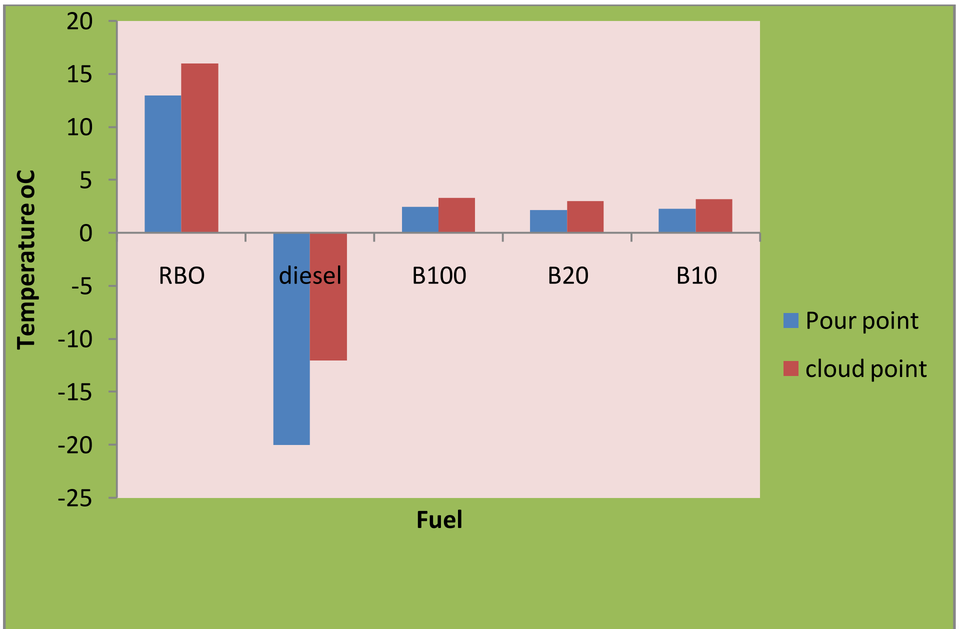

Fig. 2 Pour and cloud points

Kinematic viscosity

The kinematic viscosity of the oil is within the range for vegetable oils and decreased significantly after transesterification. It also reduced further with blending due to the diluting effect of diesel which has a slightly lower kinematic viscosity. By and large the fuel samples have kinematic viscosities that are all within the range for biodiesel as in Figure 3. Viscosity affects fuel atomization, performance and lubricity of fuel pump, penetration of injected fuel, and fuel burning efficiency. Hoekman et al., 2012 reported that the higher viscosity of biodiesel can lead to inferior atomization and spray, resulting in a larger mean liquid droplet diameter and a longer ignition delay.

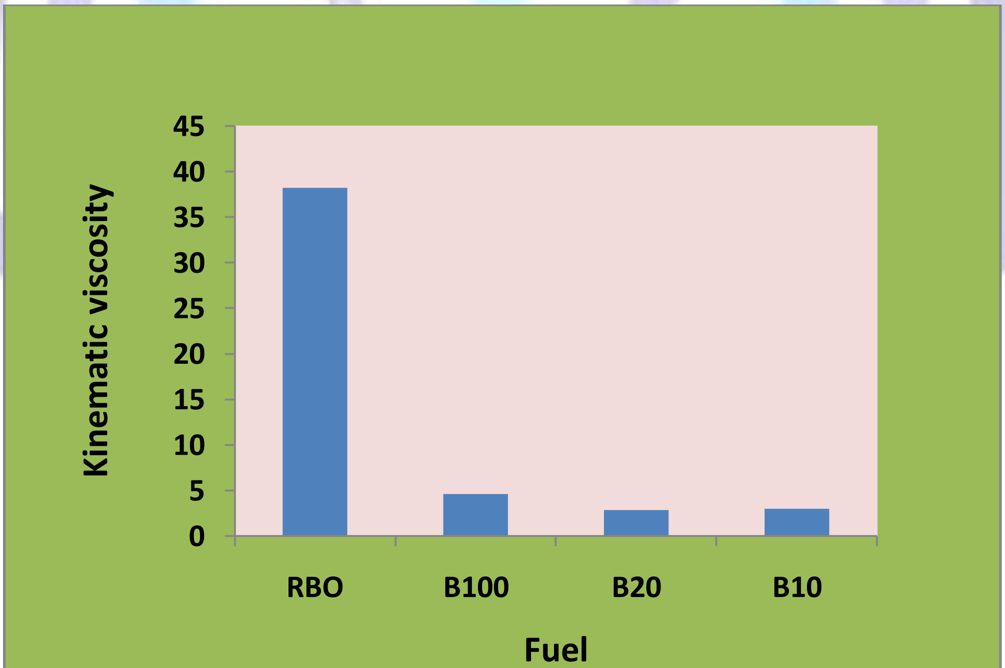

Fig. 3 Variation of Kinematic viscosity

Flash Points

The flash points reduced after transesterification and blending and the variations are not too wide. The flash points are much higher than that for diesel fuel thus making it in all its forms much safer. The variation is shown in Figure 4 and that for B100 is above the minimum limit of 130oC set by ASTM thus making it a safe fuel by the criterion. Flash point is a measure of volatility and flammability of a fuel. By vegetable oil standard, the flash point of rice bran oil is very low and enables the oil to be used directly without transesterification. That of the B100 is within the range for other biodiesels (Bello, 2011). Flash points f the blends tend toward that of diesel with increasing amount of biodiesel.

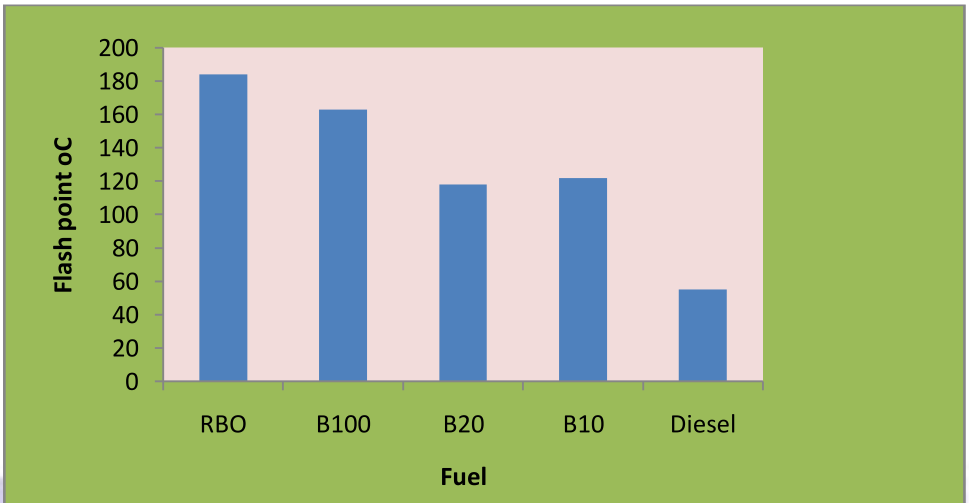

Fig. 4 Flash point of the fuels

Lower Heating Value

The lower heating value of the oil is lower than that of diesel because of the oxygen content which has low heating value and occupies about 10% of the total volume. It is however enhanced by blending with diesel that has higher value as shown in Figure 5. In general, biodiesel has lower heating values than diesel which leads to lower torque output and higher specific fuel consumption (Bello, 2011).

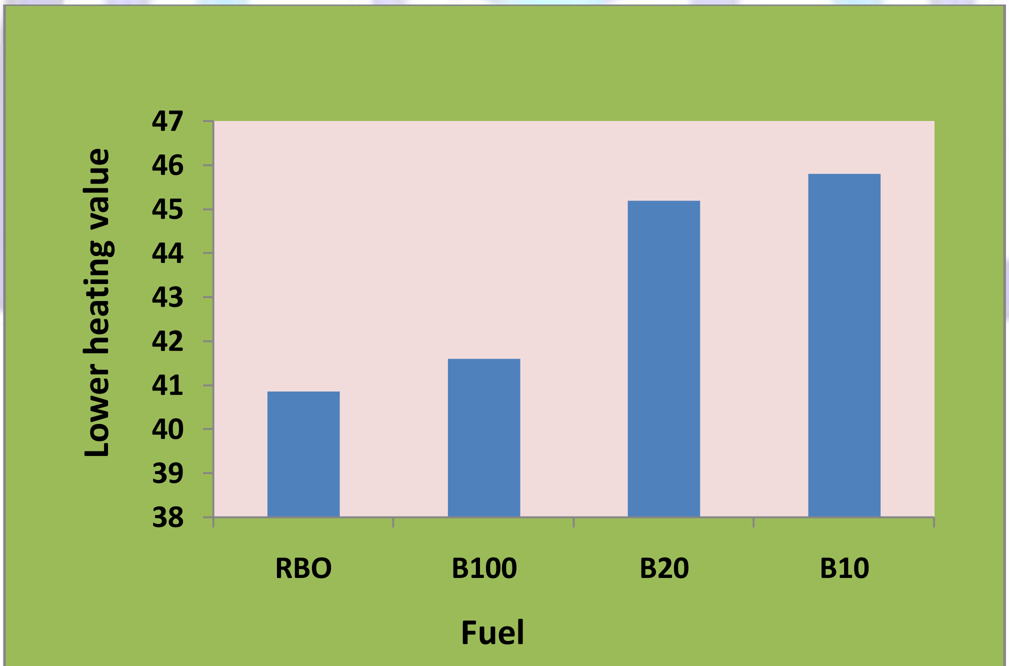

Fig. 5 Variation of lower heating value

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Cetane Index

Cetane Number (CN) is a measure of the ignition quality of diesel and biodiesel fuels and a quality index. The CN increased by 11.6% after transesterification. Again this is quite a surprise because the CN of most vegetable oil usually increase by a minimum of 50% for example castor oil 53%, pumpkin oil 70% and ground nut oil 186.6% (Bello, 2011). However, blending reduced the cetane number because of the lower value for diesel as shown in Figure 6. For diesel engine usage, it is an important factor, as it affects cold startability, idlibility and incompleteness of combustion that can increase harmful exhaust emissions.

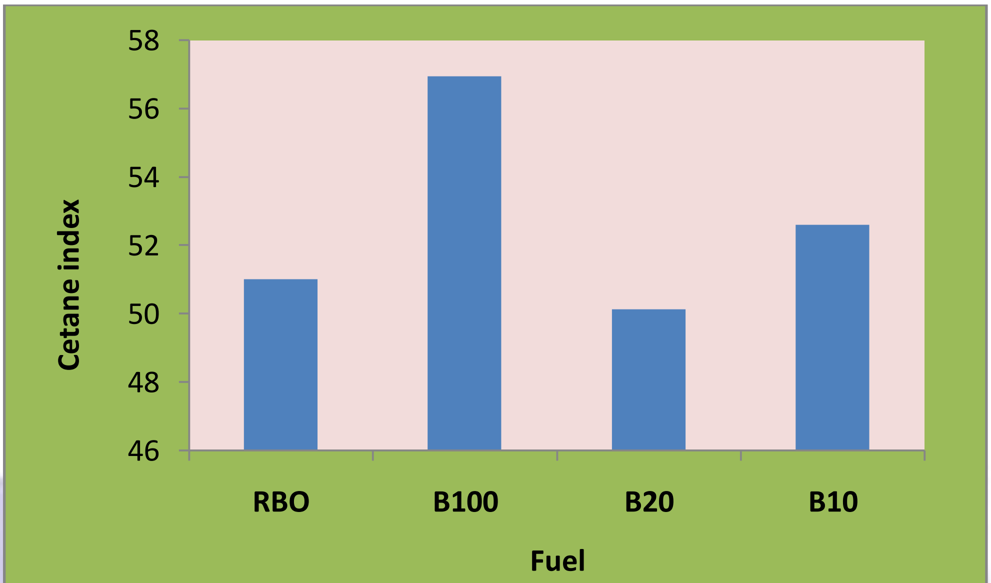

Fig. 6 Variation of Cetane index

Iodine, Peroxide and Oxidation Values

Biodiesel can oxidize during storage and handling and in the presence of heat and air, leading to the formation of peroxides, acids, gums and deposits. The iodine value increased by 8.7% after transesterification but is drastically reduced by blending because diesel is saturated. Peroxide values also follow the same pattern as shown in Figures 7 and 8 respectively. However, oxidation reduces and then increases with blending as can be seen in Figures 9. These values are important from the point of view of fuel stability in storage. High level of saturation will provide for high oxidative and thermal stability as a result of fewer vacant chains and leading to a slower deterioration rate of the lipid characteristics (Lin and Chiu, 2010). Once oxidative instability is initiated, it increases according to the peroxidation chain mechanism (Focke et al., 2010). Oxidation can be caused by several factors that includes, water content, heat and oxygen. Leading to the breakdown of unsaturated fatty acids and the formation of primary oxidation products such as hydroperoxides and conjugated dienes (Arisoy, 2008)

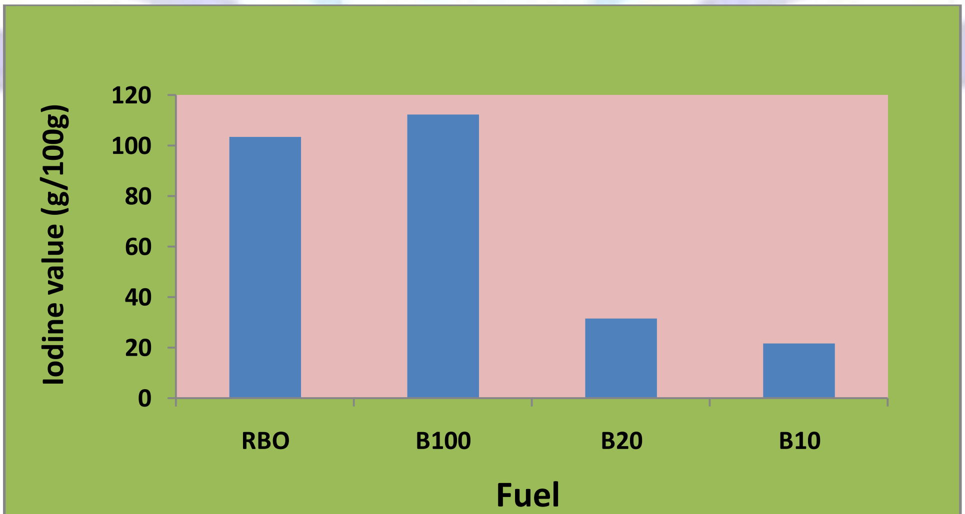

Fig. 7 Variation of Iodine value

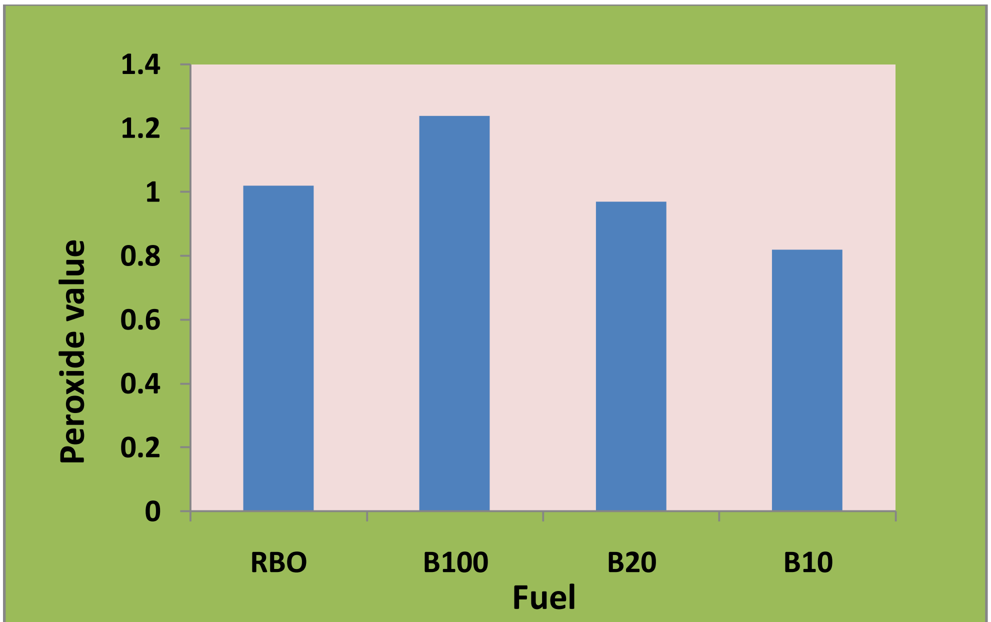

Fig. 8 Variation of Peroxide value

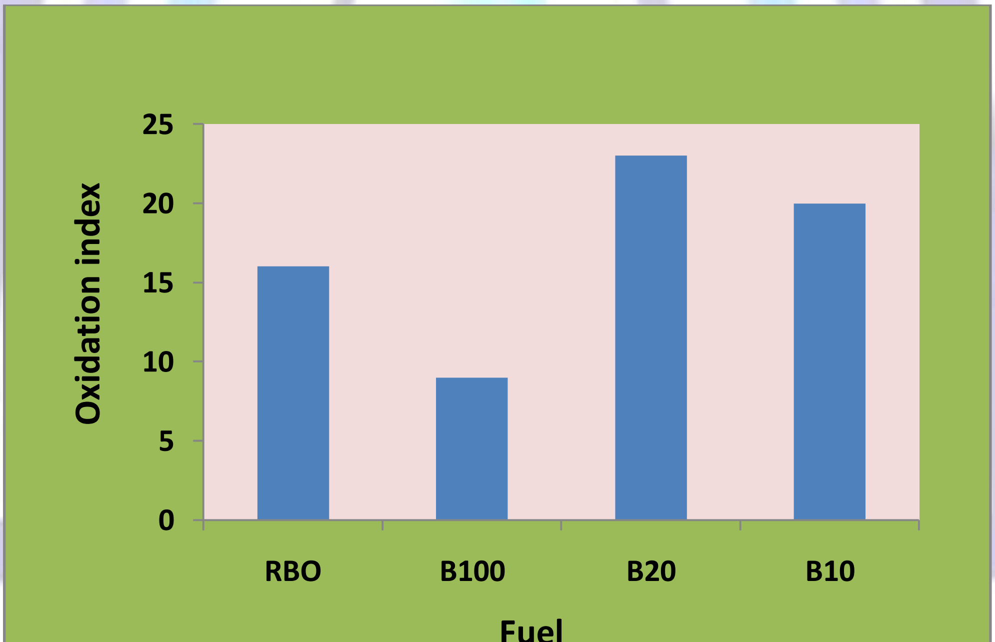

Fig. 10 Variation of Oxidation index

Saponification value and Soap Content

Saponification value increased by 9.5%, while the soap content increased significantly after transesterification due to the action of NaOH used as catalyst and incomplete purification as shown in Figures 10 &11. Soap inhibits the separation of biodiesel and glycerin fraction (Madras et al., 2004) and must be reduced if reasonable biodiesel yield is to be achieved. It is a measure of the effectiveness of the purification process of biodiesel production. High amount of soap can result in irregular combustion and thick exhaust smoke.

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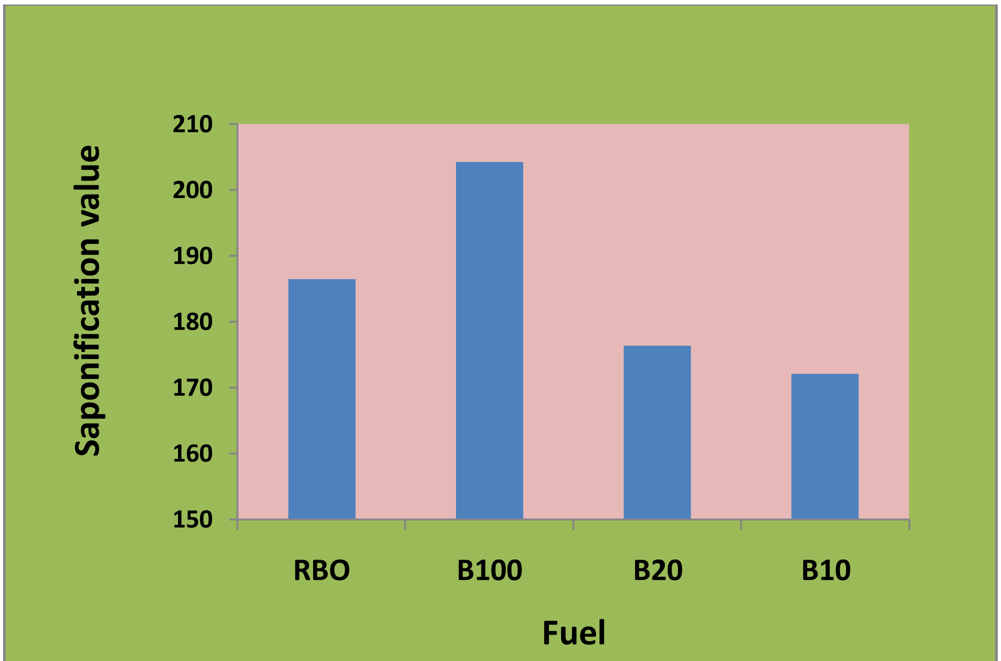

Fig. 11 Variation of Saponification value

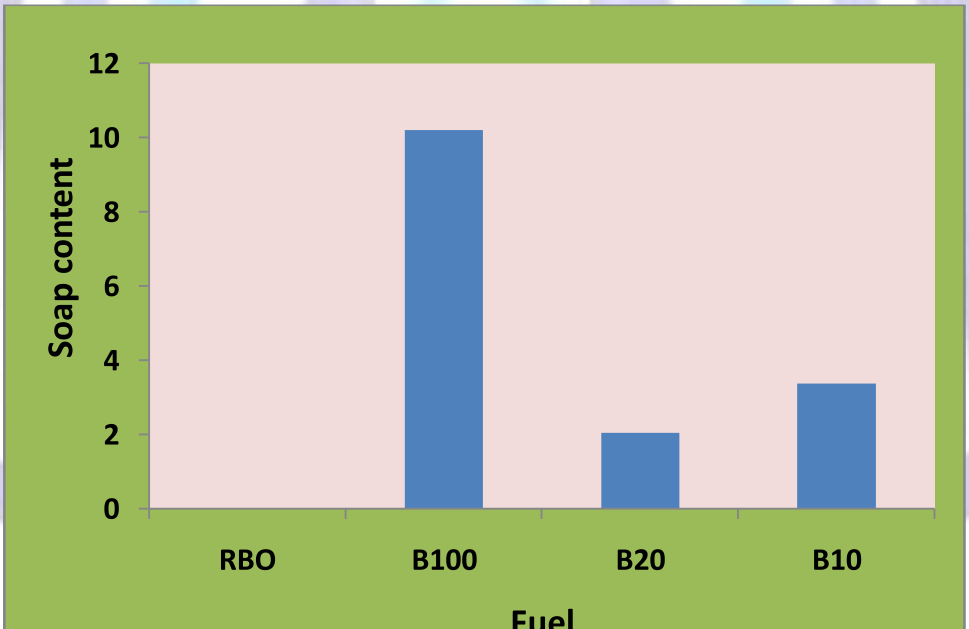

Fig. 14 Variation of Soap content

Free Fatty Acid and Acid Values

Of particular significance are the values of free fatty acids and acid values. When the acid value is above 3 mgKOH/g, it will form soap, which inhibits the transesterification process (Ramadhas et al., 2009) The values for RBO and B100 are surprisingly quite low and would hence not require pretreatment with acid to convert some of the free fatty acids to esters before transesterification. By not undergoing the pretreatment process, the cost of production can be cut considerably under industrial situations.

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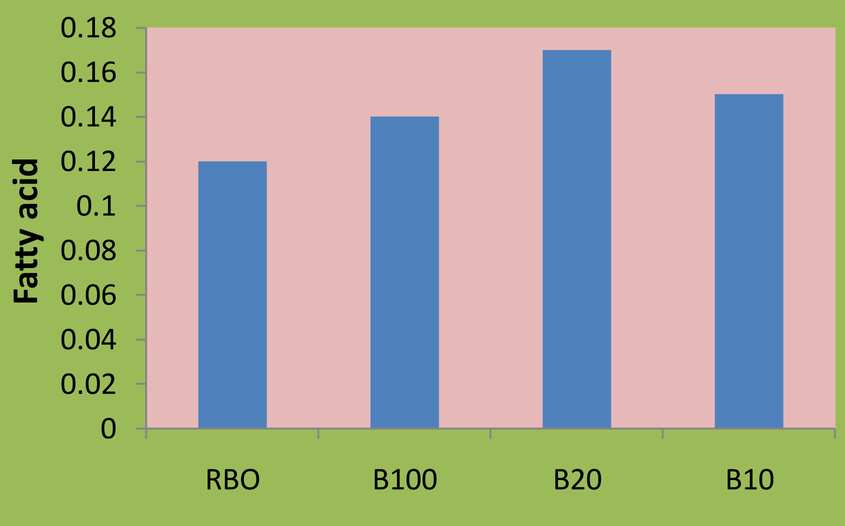

Fig. 12 Variation of Fatty acid

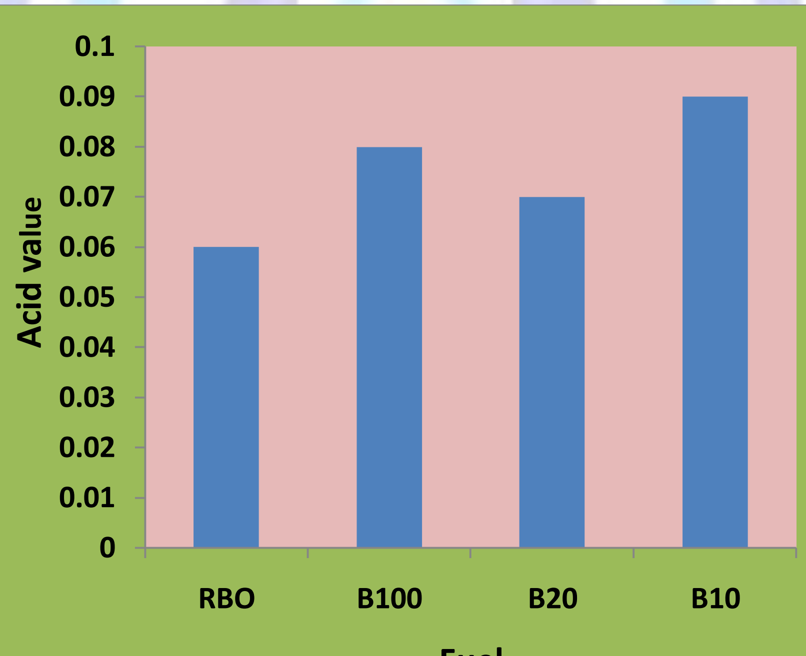

Fig. 13 Variation of Acid value

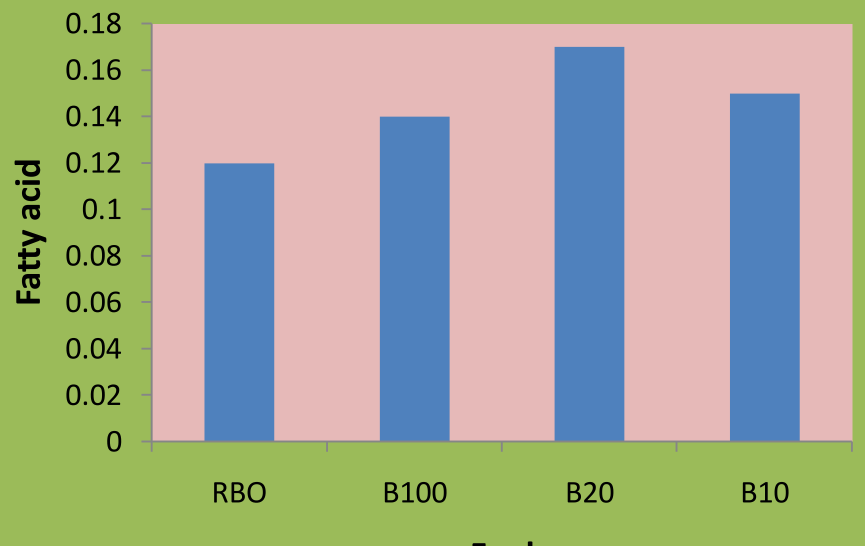

Fig. 12 Variation of Fatty acid

Water and Residue and Moisture Contents

This is the free water droplets and sediment particles in the fuel. Water and residue, and moisture contents were reduced substantially after transesterification because although the biodiesel was washed with water, it was dried in the final stage. The variations are shown is Figures 14 and 15. High water moisture content in the oil can inhibit the transesterification process. Excess water can lead to corrosion and provides an environment for microorganisms. The existence of water in liquid fuel enhances its hydrolysis, induces the formation of microorganisms resulting in the deterioration of the fuel characteristics, particularly for biodiesel. In a vehicle engine, high water content can damage fuel filter element, and cause water accumulation which at subzero temperature can form ice and block fuel flow. Sediment level can also increase as a result of oxidation of the fuel, which can increase acid value and viscosity. As shown in Figure 14, water level can be reduced to negligible level by transesterification and blending. Sediments in the fuel can block filters leading to the rapid degeneration of fuel properties such as the flash point, cetane number, and heating value. On the positive side, because of the high latent heat of evaporation of water, the engine would operate at lower temperature.

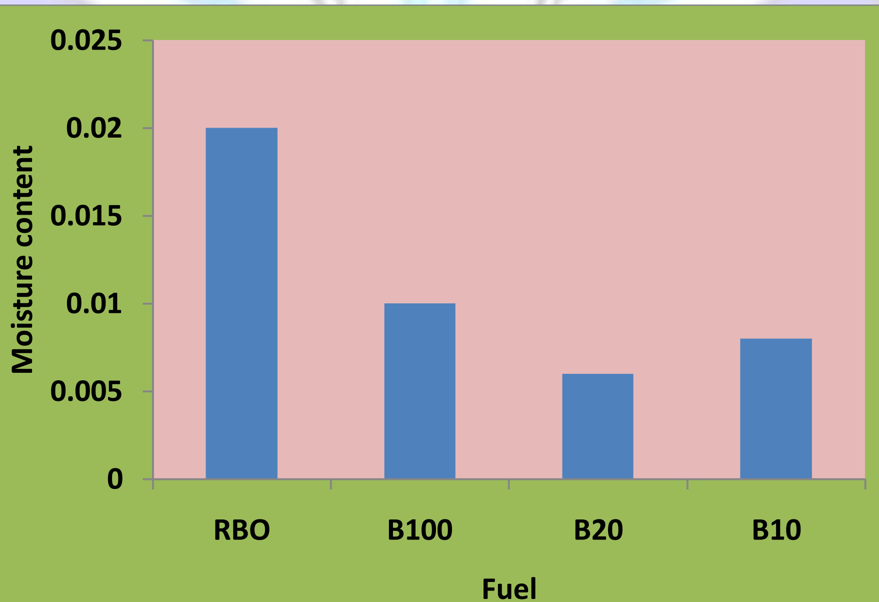

Fig. 16 Variation of Moisture content

Conclusions

Rice bran has an oil content of 20% and is highly saturated.

Rice bran oil surprisingly has a free fatty acid value of 0.12% which makes acid pretreatment unnecessary before alkaline transesterification to get reasonable amount of biodiesel yield.

Most of the properties changed with transesterification except the soap content that increased because of the alkaline catalyst used.

References

[1] Bello. E.I., Agge M., (2011a) Performance Evaluation of Egunsi Melon (*Citrullus Colocynthis L.*) Seeds oil Biodiesel. JETEAS 2(5):74-75.

[2] Bello. E.I., Agge M., (2011b) Biodiesel production from Ground Nut. JETEAS 2(5):74-75

[3] Haas M.J., Scott K.M., Marmer W.N., Foglia T.A. (2004) An effective method for the production of fatty acid esters from vegetable oils. J Am Oil Chem Soc. 81:83–89.

[4] Lin Lin A., Dong Ying A., Sumpun Chaitep B, Saritporn Vittayapadung AL. (2009) Biodiesel production from crude rice bran oil and properties as fuel. Applied Energy 86:681–688

[5] Goffman F.D., Pinson S., Bergman C. (2003) Genetic diversity for lipid content and fatty acid profile in rice bran. J Am Oil Chem Soc. 80:485–90.

[6] Hargrove KL. (1993) Processing and utilization of rice bran in United States. In:Marshall WE, Wadsworth JI, editors. Rice science and technology. New York: Marcel Dekker. p. 381–404.

[7] Ju, y., Vali S.R. (2005) Rice bran oil as a potential source for biodiesel: A review. Journal of Scientific & Industrial Research, 64:

[8] Zullaikah S., Lai C.C., Vali S.R., et al. (2005) A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. Biores Technol 96:1889–96.

[9] Pramanik K. (2003) Properties and use of jatropha curcas oil and diesel fuel blends in compression ignition engine, Renewable Energy, vol. 28, pp. 239-248.

[10] Conceicao M.M., Candeia R.A., Silva F.C., Bezerra A.F., Fernandes V.J., Souza A.G.(2007) Thermochemical Characterization of Castor Oil Biodiesel Renewable and Sustainable Energy Reviews 11(5): 964-975.

[11] Bhattacharyya, D.K., Chakrabarty, M.M., Vaidyanathan R.S, Bhatachryya A.C (1983) A Critical Study of The Refining of Rice Bran Oil. J. Am. Oil Chem. Soc, 60: 467-471.

[12] Giwa S., Abdullah L.C., Adam N.M. (2010) Investigation of Egunsi (Citrullus colocynthis L.) Seed oil as potential biodiesel feedstock. Energies 3:607-618.

[13] Goffman, F.D. (2003) Genetic diversity for Lipid Content and Fatty Acid Profile in Rice Bran. J.Am. Oil Chem. Soc. 80: 485-490

[14] Hoekman, S.K., Broch, A., Robbins, C., Ceniceros, E., Natarajan M. (2012) Review of biodiesel composition, properties, and specifications. Renew. Sust. Energy Rev., 16, 143–169.

[15] Focke, W.W.; Westhuizen, I.; Grobler, A.B.L.; Nshoane, K.T.; Reddy, J.K.; Luyt, A.S. (2012) The effect of synthetic antioxidants on the oxidative stability of biodiesel. Fuel, 94, 227–233.

[16] Arisoy, K. (2008) Oxidative and thermal instability of biodiesel. Energy Source, 30, 1516–1522.

[17] Lin, C.Y.; Chiu, C.C. (2010) Characteristics of palm-oil biodiesel under long-term storage conditions. Energy Convers Manag. 51, 1464–1467.

[18] Madras, G, Kolluru, C., Kumar, R. (2004) Synthesis of Biodiesel in supercritical Fluids. Fuel 83:2029:2033.

[19] Ramadhas, A.S., Jayaraj, S., Muraleedharan. C. (2009). Biodiesel production from high FFA rubberseed oil. Fuel (84)4:335-340.