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ORIGINAL RESEARCH ARTICLE

CHARACTERIZATION OF BLENDS OF PETROL AND BIOETHANOL SYNTHESIZED FROM NIGERIAN PALM BUNCH

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ABSTRACT

This study investigated fuel properties of pure petrol blended with bioethanol produced from Nigerian waste palm bunch. The produced bioethanol was blended with pure petrol at volume percentage ratio of 0:100, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40 and 100:0 to obtain E0, E10, E20, E30, E40, E50, E60 and E100 blend respectively. These were then characterized for fuel properties base on ASTM standard. The result confirmed that fuel properties of bioethanol produced from Nigerian waste palm bunch met the International Standard as established by ASTM for use in SI engine. The blends improved the fuel properties of pure petrol. Density of the blends increased as the percentage of bioethanol increases in the blends. Octane number of pure petrol increased with increase in bioethanol in the blends. Flash point of all the blends was below 15 oC making them susceptible to ignition and having the chance of flammability hazard. 10 % bioethanol increased the blend's vapor pressure to a peak value of 53 kPa which declined with further increase of bioethanol percentage. The bioethanol increased viscosity of pure petrol. Calorific value of pure petrol was decreased with increase in the bioethanol content.

1.0 Introduction

Bioethanol is a biofuel made from biomass and primarily used in blends with petrol, for automotive, thermal and power generation, according to quality specifications set by the American Society for Testing and Materials (ASTM), the Environmental Protection Agency (EPA), state regulatory agencies and their own producing company standards. Engines run on fossil fuels are major contributors of various types of air polluting exhaust gasses such as Particulate Matter, Carbon monoxide, Oxides of Nitrogen, Sulfur, and other harmful compounds Ashish and Mohapatra, 2013). Considering all these shortcomings of fossil fuels, there is need for an alternative fuels from biomass (Cheng et al., 2007). Biothanol has been widely encouraged as a substitute / improver for petrol to achieve emission reduction target of the Kyoto protocol (1997). Pure petrol blended with bioethanol is particularly promising since it is more readily incorporated into the existing fuel combustion system and burns cleaner (Tan et al., 2014). However, producing biofuels from biomass crops has its own negative consequences such as food price hike; soil degradation and diversion of food land (Ruth, 2008; Koonin, 2006; Anjan, 2013). According to Regmi and Mark, (2001), a 1 % increase in food prices causes an average of 0.75 % decline in food consumption in developing countries. In addition to reducing caloric intake as food prices increase, low-income people also switch to less nutritious food (Von Braun, 2007; Raneses et al., 1998). Thus, to meet the energy demand without posing trait to human food chain, bio-waste is encouraged as feedstock for producing bioethanol (Julian et al., 2011). The renewable feedstock is also abundant in nature (Tan et al., 2014). Focus is on utilizing pre-exploited agricultural land, and non food crops that are adaptive to current and foreseeable climatic conditions. This will lead to significant reduction of food price hike; soil degradation and diversion of food land. Utilizing lignocellulosic agricultural wastes which constitute approximately 50 % of all land produced biomass such as waste palm bunch will result in transformation of waste to energy (Thallada, 2011; Siddegowda and Venkatesh, 2013; Siew et al., 2009). It is estimated that bioethanol produced from the world's agri-waste and forest residues could replace 32 % of global petrol consumption (Leland, 2005). A fuel blend of different fuels is a mixture with its own unique physical characteristics which depends on the miscibility of the components and their individual properties. These can as well be influenced by other factors like production process, feedstock type and environment. Thus, fuel blends may have different effects on engine performance improving or reducing the performance (Ashish and Mohapatra, 2013; Karl et al., 2005, Chevron, 2004). In the light off the above, fuel properties of a fuel blend have to be ascertained before it is recommended for running a particular engine. This study was undertaken to investigate the fuel properties of the blend of pure petrol and bioethanol produced from Nigerian waste palm bunch.

2.0 Materials and Methods

2.1 Material Procurement and Preparation

The bioethanol was produced from Nigerian waste palm bunch collected from Siat Nigeria Ltd, Ubima, Rivers State; by pretreatment, hydrolysis and fermentation (Nuru et al., 2014, Julian et al., 2011; Lalit et al., 2011). The waste palm bunch was subjected to physical pretreatment, hydrolysis with 1.2 % dilute H2SO4, at 160 oC for 30 min, fermentation for 72 h with S.scerevisea separated from palm wine, then distillation to obtain bioethanol fuel. 99.9 % pure petrol was obtained from NNPC Port Harcourt Refining Company Limited, Elesa-Eleme, Port Harcourt Rivers State.

2.2 Fuel blends formulation and characterization

Elemental analysis of the produced bioethanol was carried out following the ASTM standard test procedures and compared to ASTM D4806 specification for denatured fuel bioethanol blend able with petrol for use as automotive SI engine fuel. The elemental properties obtained include ash content, water content, acidity, pH and purity. The bioethanol content otherwise purity of the fuel was determined according to ASTM D 5501 in a gas chromatography. Its pH was determined at room temperature using a pH meter according to ASTM D 6423. Ash content was determined according to ASTM D482; 120 mL Porcelain Crucible was heated at 700 oC for 10 min. It was cooled to room temperature in a suitable container, and weighed as (W1). The sample of 5 g quantity (W2) was poured into the crucible, ignited and allowed to burn until only ash and carbon remains. The carbonaceous residue is reduced to ash by heating in a muffle furnace at 700 oC, cooled and weighed (W3). The average percentage ash was calculated with Eqn (1).

$$\text{Ash, \%} = \frac{w_3 - w_1}{w_2} \text{ x } 100 \qquad (1)$$

The acidity was determined according to ASTM D974, using Potassium hydroxide (KOH) as the titrant. The acid number was calculated by comparing to that of a blank as given in Eqn (2).

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$$\text{Acid number, mg of KOH}/\text{g} = \frac{[(\text{A} - \text{B})\text{M x } 56.1]}{\text{W}} \qquad (2)$$

where: A = KOH solution required for titration of the sample mL, B = KOH solution required for titration of the blank, mL, M = molarity of the KOH solution, and W = sample used, g.

Water content of the bioethanol was determined based on ASTM D95. It was subjected to water content distillation using a Dean and Star distillation unit in Figure 1. 100 ml of the bioethanol was mixed with 100 ml of aromatic mixture (80 % toluene and 20 % xylene) and subjected to heat for 2 h from boiling point. The trap solution was observed for separation and changes in the presence of methyl red dye. Methyl red dye was used because it dissolves in PMS but dissolves not in water.

Figure 1: Water Content Distillation

Different blends of the bioethanol and pure petrol shown in Figure 2 were then formulated and characterized for its fuel properties according to ASTM standard procedures for petrol, bioethanol, and petrol-oxygenated fuels. The blends were E0, E10, E20, E30, E40, E50, E60 and E100 formulated in 0:100, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40 and 100:0 volume percentage of bioethanol/petrol respectively. E100 and E0 were the produced bioethanol and the obtained pure petrol respectively.

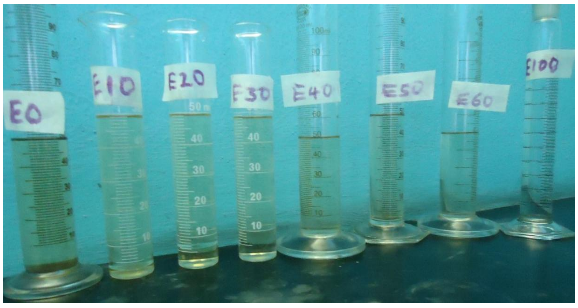

Figure 2: Bioethanol-Pure Petrol Fuel Blends

Fuel properties determined includes density determined using the weight per volume method (Tangka et al., 2011), viscosity in centipoise using capillary viscometers at a fixed temperature of 40 °C based on ASTM D 445, flash point using the Pensky-Martens closed cup tester (D 93), Vapor pressure (VP) using an auto vapor pressure tester (D 4953), distillation profile or volatility using a batch atmospheric distillation apparatus (D 86), calorific values were determined by burning a known amount of bioethanol in a Gallenkemp ballistic bomb calorimeter as described by Abdullah et al., (2011). Octane number (ASTM D 2699-86, D 2700-86) was determined using a portable cetane and octane meter, and a Comparative Fuel Research Engine (C- 48386 model) shown in Figure 3.

Figure 3: Comparative Fuel Research Engine (C- 48386 model)

The engine is of 1-stroke, 1-cylinder and operates on a fuel at a time. It consists of four carburetors, a detonation pick up, a dial indicator or micrometer, a detonator meter and a knock meter. Two carburetors are for primary fuels blend (iso-octane and n-heptane) and two for sample fuel that need or need not temperature conditioning respectively before combustion. 1000 ml of the sample was poured into the carburetor to ensure that the fuel level is within 0.7 – 1.7 range in the carburetor sight glass. The detonation pick up threaded to the cylinder; has a sensor exposed to combustion chamber pressure and sends same to the detonation meter as voltage signal proportional to the rate of pressure change. The detonation meter being a signal conditioning equipment accepts, amplifies and then sends it to the knock meter. The knock meter, a 0 – 100 strip chart recorder displays the signal as knock intensity. The dial indicator displays the cylinder height with respect to the piston. The octane number was determined using the bracketing procedure (ASTM 2699); here, the knock meter reading was bracketed at constant compression ratio between knock meter readings for two reference fuels (i.e. 90 and 92 primary reference fuels), and the sample rating was calculated by interpolation. Cylinder height was adjusted thereby varying the compression ratio, by a screw attached to each of the carburetors while reading was taken at knock meter display of ‘50’ to ensure a reliable result. This reading was then compared with the ASTM guide table for the corresponding octane number at the standard knock intensity for the specific fuel.

Drivability index (DI) of the blends which is its quality of being drivable, of being easy or pleasant to drive. In other words, DI of the blends give insight on how they response to the drivers demand and driving comfort. Drivability index is based on the relationship between the distillation temperature of the fuel and the cold start and warming up parameters of the vehicle. Lower values of DI generally result in better cold-start and warm-up performance, but once good drivability is achieved, there is no benefit to lowering the DI further. According to Renewable Fuels Association (2010) and Chevron (2009), DI can be calculated using Eqn (3).

$$\mathrm{DI}\ (^{\circ}\mathrm{C}) = 1.5\mathrm{T}_{10} + 3.0\mathrm{T}_{50} + 1.0\mathrm{T}_{90} + 1.33(\mathrm{ethanol}\ \%) \qquad (3)$$

where: T is distillation point temperature at 10 ml, 50 ml and 90 ml respectively.

Distillation was determined with 100 ml of each fuel samples distilled to observe its volatility. The distillation was performed According to ASTM D 86 in a batch atmospheric distillation apparatus HDA 620 model (Figure 4) at ambient pressure. Systematic observations of temperature readings and volumes of condensate were made. The initial boiling point, IBP, end boiling point, EP and total distillate TD were determined to plot their distillation profile curves presented in Figure 1 under Results and Discussion.

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Figure 4: Atmospheric Distillation Apparatus (HDA 620 model)

3.0 Results and Discussion

3.1 Characterization Data

Elemental analysis obtained for the bioethanol is presented in Table 1 while fuel properties of the blends are presented in Table 2 and discussed below it with Figure 3 – 7. Table 1 satisfies ASTM D4806 requirement thereby confirming the produced bioethanol blend able with pure petrol. All petrol blend able with ethanol shall meet a minimum 50 % evaporated distillation temperature of 77°C (170°F) prior to blending with the ethanol (ASTM 4808). Table 2 shows that the formulated blends fall within the qualities usable in SI engine according to ASTM D4814 requirement, as they improved fuel properties of the pure petrol in the blends.

Table 1: Elemental Analysis of the Produced Bioethanol Fuel

Parameters	E100	ASTM Range	ASTM Method
Purity %	97.68		D 5501
Ash content %	0.03	0.05	D 482
H2O content (% vol)	0.42	1.0 (% vol) or 1.26 mass %	D 95
Acidity	5.05 mg/L	0.007 % mass or 56 mg/L (max)	D 974
pH	6.61	6.5 – 9.0	D 6423

Table 2: Fuel Properties of the Formulated Blends

Parameters	Sample Fuel								ASTM Method
	E0	E10	E20	E30	E40	E50	E60	E100	
Density(kg/m^3)@15 °C	744.73	747.65	752.7	759.93	768.89	777.64	782.5	791.13	D 4052
Viscosity @ 40 °C (centipoise)	0.6097	0.6508	0.7132	0.9636	0.9951	1.3835	1.3592	1.6692	D 445
Octane Number	89.2	91.8	93.4	95	96.5	98.8	100	124	D2699
VP (kPa)	48.1	53.0	42.1	42.4	44.0	41.7	36.8	13.043	D 4953
Flash pt, °C	-69	-38	-27	-18	-13.2	-8.7	-4.8	12.8	D 93
Calorific value (MJ/kg)	43.62	41.81	40.22	38.54	37.03	35.36	33.73	29.16	D 240
Drivability Index (°C)	723.84	704.51	588.56	615.31	622.68	539.69	532.57	589.51	D 4814

Table 2 shows that densities of the sample fuels increased from 744.73 kg/m^3 for pure petrol to 782.5 kg/m^3 for E60 while the produced bioethanol E100 has 791.13 kg/m^3 density making

6.23% increment. E100 has higher density than pure petrol and increased the density of its blends with pure petrol. As the percentage of bioethanol in the blend increased, the blend became denser. Pure petrol density increased by 0.39 %, 1.1 %, 2.04 %, 3.24 %, 4.42 %, 5.07 % respectively with E10, E20, E30, E40, E50 and E60. Density is the basic gauge of fuel adulteration, and is indirectly related to temperature. Fuel density has the greatest impact on fuel capacity (Donig, 2008). So, it is advice to 'tank up' vehicles in the morning and evening when fuel is denser with small volume, to get more value for money spent. Since fuel is sold volumetrically, higher density promises greater potential energy. Reported density of the produced bioethanol being 767 kg/m^3 is less than 785 kg/m^3 from Potato waste by Talal et al., (2010); 789 (kg/m^3) from Sugar cane-palmwine-raffia trunk by Nwufor et al., (2014), and Maize-raffia wine-palmwine by Tangka et al., (2011).

The Kinematic viscosity of the bioethanol fuel at 40 °C is higher at 1.6692 centipoise compared to petrol which is 0.6097 centipoise (Table 2). Viscosity, a strong function of temperature affects fuel flow and amount atomized on pumping and injecting (Viele et al., 2014). If fuel viscosity is high, the injection pump will be unable to supply sufficient fuel to fill the pumping chamber, causing poor atomization and a loss in power (Van et al., 2004). Lower viscosity causes smaller diameter of the droplets in the spray. Below certain limits, low viscosity increases the leaks in the fuel system. Adding bioethanol to petrol increased its viscosity with increase in bioethanol percentage in the blend. However, fear of poor atomization and leaks associated with high and low viscosity respectively is ruled out with lower bioethanol content. 1.6692 viscosity reported for the produced bioethanol in Table (2) is higher than 1.1 reported by Talal et al., (2012).

The octane number of the fuels reported in Table 2 was measured to be 124 for the product bioethanol which is higher than 89.2 for pure petrol with 39 % increment. The octane number of pure petrol increased continuously and linearly with percentage increase of bioethanol in the blends to 100 in E60. This could be because of higher oxygen content and octane number of the product bioethanol fuel resulting to a gradual shift from normal heptane (C_7H_{16}) to ideal iso-octane (C_8H_{18}) of the blends. Pure petrol having lower octane number and higher calorific value will burn faster than the bioethanol and its blends having lower calorific value and higher octane number. Notwithstanding, octane number being a measure of the ignition quality of a fuel of which high octane number means more efficient ignition and consequently higher engine performance, proves that the presence of bioethanol in the blends will improve petrol engine performance as the octane number increased with increase in bioethanol in the blends. Therefore, the fear of auto-ignition and knocking effect could be ruled out in the utilization of these blends. This suggests the product bioethanol as an effective agent for increasing the value of petrol octane number. Octane number of 124 reported for E100 is higher than 108.6 and 114 but lower than 129 recorded by Talal et al., (2010), Nwufor et al., (2014) and Tangka et al., (2011) respectively.

As reported in Table 2, Vapor pressure of the product bioethanol is 13.043 kpa which is 72.9 % lower than 48.1 kPa for the petrol. Vapor pressure is a measure of "front end" volatility, and a fuel with extremely high vapor pressure may cause problems with hot start ability, hot drivability and vapor lock protection (Karl et al., 2005; Chevron 2004). Allowable RVP for petrol is 0.7 bar (70 kPa) in summer and 0.9 bar (90 kPa) in winter (at 37.8 °C) (RFA, 2002). 10 % bioethanol in pure petrol increased its RVP to a peak value of 53 kPa suggesting that it could reduce the risk

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for a flammable mixture forming than other blends. Table 2 clearly shows that further increase in the bioethanol above 10 % declines the blend vapor pressure and the decrease is not linear. Product bioethanol has fewer highly volatile components than pure petrol which suggest that it will have less emissions resulting from evaporation. However, when added to pure petrol, the vapor pressure of the blend was increased thereby increasing evaporative emissions. This could be because in its pure form, bioethanol molecules are polar and bond to each other via the hydroxyl (OH) groups. These forces of attraction prevent the molecules from leaving the liquid but in the presence of hydrocarbons, the bonding was weakened. It is expected that at a point addition of bioethanol will not further boost the vapor pressure. It can also be deduced that bioethanol contents higher than 40 % will increase the risk that vapor will form with pressures under the upper flammability limit. However, the blends ensure products of suitable volatility performance. VP of 13.043 kPa reported for E100 is higher than 9 and 9.5 but lower than 48 reported by Tangka et al., (2011), Nwufor et al., (2014) and Talal et al., (2010), respectively.

The observed flash point of produced bioethanol (Table 2) is 12.8 °C while other blends has flash point below 10 °C. Flash point indicates the lowest temperature at which the vapor overhead the sample is ignitable with the application of an ignition source under specified test conditions. It predicts the temperature at which the vapor pressure reaches the lower flammable limit. Flammability limits is the maximum and minimum concentrations of combustible vapor in the air and the temperatures at which the vapor occurs, that will propagate a flame after sufficient ignition energy is provided (RFA, 2009, 2002). The result presented in Table 2 shows that all the blends are susceptible to ignition and has the chance of flammability hazard. The flash point of the bioethanol is high compared to -69 °C for petrol, indicating that it is safer than petrol regarding its handling, transportation and storage. Increase in bioethanol percentage continuously increased the flash point of pure petrol from -69 °C to -4.8 with 60 % bioethanol. Thereby increasing its safety handling, transportation, storage and flammability limits. High flammability limits promotes safety handling of fuel (RFA, 2009, (Ashish and Deshmukh 2012). Flash point of E100 which is 12.5 °C agrees with Nwufor et al., (2014) and Tangka et al., (2011) but Talal et al., (2010) that reported 14 °C.

Calorific values of the pure and blended fuels are presented in Table 2. Calorific value or heat of combustion is a measure of the energy available from a fuel. Knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat. The calorific value of the product bioethanol was found to be 29.16 MJ/kg while that of pure petrol is 43.62 MJ/kg on weight basis. For the product bioethanol (E100), calorific value is 31.73 % less than that of pure petrol. It is deduced from the Table that the calorific value of the petrol blend steadily decreased as bioethanol content increased. It decreased to 33.73 MJ/kg in E60. This means that the consumption of blends could be higher than petrol for a driving range (Dhanapal et al., 2010; Wallner et al., 2009). However, this can be partly offset by the higher Octane Number of the bioethanol. Calorific value of 29.16 MJ/kg reported for E100 is higher than that recorded by Talal et al., (2010) and Tangka et al., (2011) but within the same range as the 29.78 MJ/kg from Nwufor et al., (2014).

The drivability index of pure petrol (Table 2) was found to be 723.84 °C, and reduced with the presence of the bioethanol but not linearly. Drivability index is a measure of the volatility characteristics of a fuel and high DI is normally associated with low volatility (RFA, 2002; Chevron, 2009). Pure petrol has the highest DI compared to other fuel samples while E60 has the least with 532.57 °C proving that pure petrol is less volatile and E60 is most volatile. Also, since low drivability is preferable in an engine, it means the bioethanol improved drivability and volatility of pure petrol and thus its cold start and warm up performance. High DI causes poor fuel evaporation in cold start, leading to lean A/F ratio, unstable combustion, HC emission, piston and cylinder wear especially in carburetors (RFA, 2010; Chevron, 2009). This is normally offset by automatic increase in injected fuel or choking in carburetor to achieve a rich mixture which results to more HC emission (RFA, 2010). Therefore, engine need to be warmed up for at least 10 – 15 minutes to bring it to its normal operating condition (Wallner, 2009).

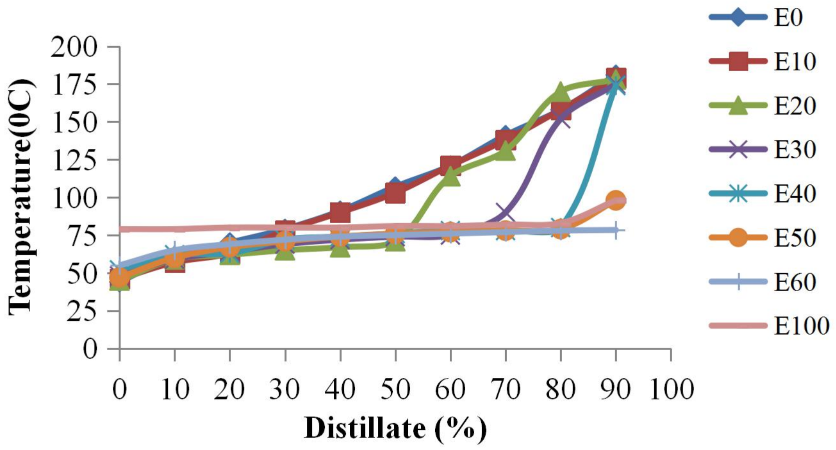

Figure 1: Effect of Blends on Distillation Profile

Figure 1 presents the distillation profile of the sample fuels from their initial boiling point (IBP) to 90 % distillate. The distillation profile (volatility profile) for the produced bioethanol showed IBP of 79 °C, 99 °C at 90 %vol and EBP of 101 °C with total distillate of 97 % vol while petrol has IBP of 44 °C, 181 °C at 90 % vol and EBP of 205 °C with total distillate of 98 % vol. Temperature of pure petrol when 10 % was distilled is 61 oC (i.e. T10), with respect to this temperature E10, E20, E30 and E50 decrease by 6.56 %, 3.28 %, 3.28 %, and 1.64 %, while E40 and E60 increased by 1.64 % and 6.56 % respectively. Decrease of 3.74 %, 36.64 %, 30.84 %, 28.97 %, 28.97 % and 29.91 %, was observed with E10, E20, E30, E40, E50 and E60 respectively for T50 (107 °C), while decrease of 1.1 %, 1.66 %, 3.31 %, 3.87 %, 45.86 % and 56.69 %, respectively at T90 (181 °C). Compared to pure petrol, the distillation curve for each blend was significantly depressed between T10 and T50 distillate. The curve depression could be attributed to the presence of the bioethanol in blends which increased its volatility. This may expect problem with cold starting and vapor lock. The resulting T10 is sufficiently low to allow enough fuel to evaporate and form a combustible mixture. T50 point associated with engine warm up; is sufficiently low to allow the engine to warm up and gain power quickly without stalling. T90 associated with the crankcase dilution and fuel economy; is not expected to be high. If T90 is too high, the larger fuel molecule will condensate on the cylinder liners and pass into the lubricating oil in the crankcase instead of burning; this will then be avoided with the blends. Blending pure petrol with the bioethanol increased the volatility, decreases the 50 % distillation point T50, affects the driveability index and also improved its fuel quality. Distillation profile of 79 - 101 °C reported for E100 is higher than 55 – 68 reported by Nwufor et al., (2014).

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Though, the product fuel has lower density and consequent lower potential energy than pure petrol, its high viscosity which rules out poor atomization; and its high octane number which means more efficient ignition and consequent higher engine performance suggests it an effective compound for improving petrol fuel quality and recommends their blends for use in spark ignition engines. This means that engines optimized for bioethanol can be more energy efficient than engines that are currently optimized for petrol (Wallner et al., 2009). The formulated blends fall within the qualities usable in SI engine according to ASTM D4814 requirement, as it improved fuel properties of the pure petrol in the blends presented in Table 2.

4.0 Conclusion

This study produced bioethanol from Nigerian waste palm bunch by physical pretreatment, chemical hydrolysis and using a catalyst extracted from palm wine in the fermentation process. The produced bioethanol characterized according to ASTM standard was found to be blend able with pure petrol and the blends are usable in SI engine. It can then be concluded that Nigerian waste palm bunch can be treated to produce bioethanol, a reliable fuel to improve pure petrol fuel properties and engine performance, and thus can be a perfect replacement for lead compound used as an anti-knock agent. The project falls under the focus category of waste to energy as it addressed issues relating to conversion of waste which poses a disposal burden to energy.

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