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Strictly as per the compliance and regulations of:

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I. Introduction

The quest for biofuel production in Botswana is derived from several factors including volatile oil prices, potential for job creation, fuel security and economic diversification. The desire to establish national energy self-reliance and to develop alternatives to finite fossil fuel resources have resulted in the development of fuel technologies that are based on the use of renewable agriculture based materials as feedstocks. In the case of renewable fuels for compression ignition (diesel) engines, the majority of efforts to date have focused on biodiesel, which consists of alkyl esters of fatty acids found in agricultural acylglycerol - based fats and oils. Biodiesel can be produced from any material that contains fatty acids, whether bonded or free (Vicente et al., 2004). Consequently, different vegetable oils can be used as fuel or feedstock for biodiesel production depending on oil properties.

All vegetable oils and animal fats consist primarily of triglycerides (Srivastava and Prasad, 2000; Karmakaret al., 2010). Triglycerides have a three-backbone with a long hydrocarbon chain attached to each of the carbons. The differences between oils from different sources relate to the length of the fatty acid chains attached to the backbone and the number of carbon–carbon double bonds on the chain. Most fatty acid chains from plant oils are 18 carbons long with between zero and three double bonds (Misra and Murthy, 2010). Fatty acid chains with no double bonds are said to be saturated and those with double bonds are unsaturated. The number of carbon atoms and double bonds in each of the five most common fatty acid chains found in common oils and fats are shown in Table 1.

The presence of double bonds in the fatty acid chains has a significant effect on the properties of the methyl esters (Knothe, 2005). The deformation of the molecule caused by the double bonds inhibits the growth of the crystals and this lowers the methyl ester's freezing temperature. Saturated oils and fats tend to freeze at higher temperatures. Animal fats, hydrogenated vegetable oils, and some tropical oils such as palm oil and coconut oil contain approximately 35 – 45% saturated fatty acids and may be solid at room temperature (Misra and Murthy, 2010). Fatty acid methyl esters (FAME) produced from such oils may gel at relatively high temperatures. The carbon–carbon double bonds in unsaturated oils and fats are prone to oxidation by oxygen in the air.

This effect is severe when the bonds are conjugated (two double bonds separated by two single bonds) as is the case for linoleic and linolenic acids. These fatty acids will oxidise 50–100 times faster than oleic acid with an unconjugated double bond. Saturated fatty acids are not subject to this type of oxidative attack. The choice of oil feedstock determines the resulting biodiesel's position in the trade-off between cold flow, oxidative stability, and cetane number. Fatty acid methyl esters from more saturated feedstock will have higher cetane numbers and better oxidative stability, but will have poor cold flow properties. Fatty acid methyl esters from oils with low levels of saturated fatty acids will have better cold flow properties, but lower cetane number and oxidative stability (Refaat, 2009).

Engine performance profile generated using a straight vegetable oil as fuel is another important property. The nature of fatty acids largely determines their ability to burn correctly in an engine (Aluyor et al.,

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2009; Moser et al., 2009). In addition, iodine value is another important property with regards to the use of straight vegetable oil as fuel or feedstock for the production of biodiesel. The iodine value indicates the degree of unsaturation of oil (number of double and triple bonds). It corresponds to the number of grams of iodine absorbed by 100 g of oil. The more the oil is unsaturated, the higher is its iodine value. As such, low iodine value (saturated oil) is propitious to good combustion (Sidibe et al., 2010). Generally, saturated oils offer better combustion (short evaporation time, short ignition delay, fewer deposits) than unsaturated oils. Overall, quality of combustion decreases with increase in degree of unsaturation.

Using straight vegetable oils in diesel engines is not a new idea. Rudolf Diesel first used peanut oil as a fuel for demonstration of his newly developed compression ignition (CI) engine as far back as 1910 (Balat and Balat, 2008) Literature suggests that vegetable oils can substitute for mineral diesel if reduction in viscosity is achieved by blending it with diesel or by preheating. De Almeida et al (2002) used heated palm oil as fuel in a diesel generator. The study revealed that carbon monoxide (CO) emissions increased at higher loads. This was due to lack of oxygen at higher equivalence ratios. Palm oil nitrogen oxide (NO_x) emissions were however relatively lower than mineral diesel. Masjuki et al. (2001) used preheated palm oil to run a CI engine. Better spray and atomization characteristics were obtained due to reduction in the viscosity of fuel due to the preheating processes. Torque, brake-power, specific fuel consumption, exhausts emissions and brake thermal efficiency were reported to be comparable to those of mineral diesel Wang et al. (2006) also performed experiment on blended vegetable oil with diesel. The authors reported higher exhaust gas temperature with very small variations in CO emission levels and relatively low NO_x as compared to diesel.

This work evaluated chemical properties and engine performance of birrea plant oil to assess potential for use as fuel and feedstock for biodiesel production in Botswana. Birrea tree is indigenous to most parts of Southern Africa. In Botswana, for example, it is widely distributed all over the country but concentrated in the north eastern part of the country, approximately 250 km north east of Gaborone, Botswana's capital city. The species then covers a huge part of the Central district and Tshapong Sub district. At maturity, the plant (tree) can grow up to approximately 10m tall with a sterm diameter of approximately 0.8 m and have several branches that bear fruits during the rainy season (October to April). However, because of limited scientific data, the age of the birrea plant (tree) from which plant oil used for this study was extracted is not covered in the present investigation. It is the author's view that some of these plants could be as old as 70 years and above but they still bear fruits. The tree grows in warm and dry climatic conditions, and produce oval fruits that turn pale yellow when ready for harvesting. In Botswana the harvesting period usually starts from December to the end of March. The fruit consists of a hard woody seed covered by pulp and juice which makes the fleshy part of the fruit. The hard seed contains mostly two oil rich nuts (kernel) which can be eaten as a snack. There is now a worldwide trend to explore wild plants for oil to augment the already existing sources of oil. The fact that the birrea tree grows in drier parts where common oil seeds cannot thrive has stirred interest in it as a valuable source of biodiesel feedstock. This has led to the evaluation of birrea nut oil as potential feedstock oil for biodiesel production. In evaluating the potential use of oil for this purpose, the fatty acid profile plays an important role.

II. Materials and Methods

a) Birrea plant oil

The birrea plant oil used for the current study was purchased from Kgetsi Ya Tsie, a Community Trust located in the eastern part of the country approximately 300 km east of Gaborone City. The primary objective of the trust is to promote the economic and social empowerment of rural women in the Tswapong Hills of Eastern part of Botswana, who extracts birrea plant oil mostly for cosmetic markets in Europe and America. Prior to the plant oil extraction processes, individuals members of the trust harvest yellow birrea fruits and manually remove the outer skin of the fruit. The hard woody seed is then dried under natural conditions for 6 to 8 weeks. The primary objective of drying the hard woody seed is to ensure that minimum force is applied on cracking the hard woody nut cover and to minimise damage of the oil rich nut. When the drying process is considered to be complete, the hard woody seeds are stored in a dry place followed by the cracking process. The cracking process is also done manually by individual members of the trust group. After cracking, the nuts are collected to a central oil pressing centre for oil extraction process.

In the present investigations birrea oil nuts from the Lerala village and communities within the out skirt of Lerala village approximately 300 km east of the Gaborone City was used to extract oil. The extracted oil was then bottled into a glass container, placed in a cooler box with ice gel and transported to the laboratory for chemical analysis as described in section 2.2.

b) Oil characterization

The composition of birrea plant oil was analysed using the Waters GCT premier Time of Flight (TOF) mass spectrometer (MS) coupled to the Agilent 6890N gas chromatograph (GC) system. The instrument has high sensitivity and fast acquisition rates. In addition, the National Institute for Standards and Technology (NIST) developed Automated Mass Spectral Deconvolution and Identification System

(AMDIS) software package, (chemdata.nist.gov/mass-spc/amdis) was used for peak identification. AMDIS extracts spectra for individual components in a GC-MS data file and identifies target compounds by matching these spectra against a reference library, in this case the NIST library. AMDIS also allows creation of personal libraries where routine analyses of compounds is encountered.

i. *Gas Chromatograph Conditions*

1 µL of birrea plant oil sample extract was injected into the system using an auto-injector. The injector temperature was set at 260^0C in the splitless mode. Helium was used as the carrier gas at a flow rate of 1ml/min. Separation was achieved using a 30 meter DB5 – MS column. The oven temperature was kept at the initial 100^0C for 2 minutes, and then gradually increased from 100^0C to 290^0C at a rate of 10^0C per minute. The total run time was approximately 35 minutes.

ii. *Mass Spectrometer Conditions*

The mass spectrometer (MS) conditions that were employed were a positive polarity of electron ionization (EI), a source temperature of 180^0C, an emission current of 359µA. Other MS conditions including electron energy, resolution were set by the system auto tune function. Detection was by the micro channel plate detector (MCP) whose voltage was set at 2700 V. The oil composition was identified and quantified using the NIST (2005) mass spectral library using a combination of the Masslynx acquisition /data analysis software and the AMDIS by NIST.

c) *Engine performance analysis*

The engine performance test was conducted on a TD43F engine test rig. The test rig is water cooled, four-stroke diesel engine that is directly coupled to an electrical dynamometer. In addition to the conventional engine design, the engine incorporates variable compression design feature which allows the compression ratio to be varied from 5:1 to 18:1.

To establish that engine operating conditions were reproduced consistently as any deviation could exert an overriding influence on performance and emissions results, the reproducibility of the dynamometer speed control set points were maintained within ± 0.067 Hz of the desired engine speed. The experimental work began with engine run on pure diesel fuel. This was done to determine the engine's operating parameters which constitute the baseline that was compared with the subsequent case when the birrea plant oil was used as fuel. At the point of fuel change, the fuel lines were cleaned with pure diesel fuel and engine left to operate with the fuel under test for approximately 15 minutes to stabilise at its new condition before readings were recorded.

III. Results and Discussions

a) *Birrea plant oil characterization*

Five birrea plant oil samples were tested to establish the chemical composition present. This was done by injecting oil sample into the GC-MS system in quantities and procedure specified in Section 2.2 in a systematic study. A reference sample prepared by AccuStandards was used to calibrate the equipment. The Fatty Acids detected from the five birrea oil samples were largely similar. For simplicity, average concentration levels of fatty acids detected are presented in table 2. Table 2 also shows a number of fatty acids recorded in birrea plant oil which were not present in the reference sample.

The Fatty Acid profile of birrea plant oil indicates a range of fatty acids and esters, the majority of which were not found in the reference sample. The observation may be attributed to the uniqueness of this indigenous and unknown plant oil. Olein 2-mono and Olein 1-mono fatty acids were identified as geometrical isomers of the same compound. Oleic acid, 3-hydroxypropyl ester is very unique in that it is not found on the NIST library and has generated a lot of interest to the authors for further research work. The fatty acid that was detected to be most abundant is Trans-Oleic acid but could not be quantified because of its absence from the reference sample. The second highest peak detected is for Ethyl oleate (ethyl ester). Other compounds had substantial presence which could improve if concentrated through processing. The composition of birrea oil recorded in this analysis is largely consistent with results obtained by other researchers (Burger et al., 1987). As discussed in Section 1, the fatty acid parameters that have the greatest impact on fuel properties are the average chain length and the degree of unsaturation. To a large extend, fuel properties improve in quality with increase in carbon chain length and decrease as the number of double bonds increase, except cold flow properties. According to Knothe (2005), the optimal fatty acid profile that provides optimal fuel properties with relatively less adverse impact on the environmental is a mixture consisting of methyl oleates, esters derived from palmitic, oleic, and decanoic acids. The fatty acid mixture of birrea plant oil presented in table 2 is largely composed of these desirable compounds, depicting characteristics of a good fuel. This stimulated the need to perform thermal performance of birrea plant oil as fuel on a variable compression ignition engine. The performance results are presented and discussed in Section 3.2.

b) *Engine performance analysis*

Prior to using birrea plant oil as fuel in the compression ignition engine, the oil was neutralised using sodium hydroxide in order to minimize the possible effects of corrosion on engine parts. The oil was also filtered to eliminate possible presence of suspended matter that could form carbon deposits in

Global Journal of Researches in Engineering (A) Volume XII Issue I Version I January 2012

the engine during combustion. The birrea plant oil was then used to power a variable compression ignition engine to test the engine performance of the fuel. Engine performance tests were conducted for compression ratios 13:1 through 17:1. To enable the main findings of the study to be identified clearly, only performance results for compression ratio 16:1 are presented in Section 3.2.1. The results were compared with the results for pure diesel fuel of boiling point 422 K, vapor pressure of 53 Pa, density of 860 Kg m^{-3} and cetane number of 48. The comparison was done on the basis of engine torque, engine brake power, and specific fuel consumption as mentioned earlier. The experimental data were collected as discussed in section 2.3, leading to the results presented in figure 1.

i. *Engine Performance Results*

Typical results for the variation of the engine torque, brake power and specific fuel consumption for birrea plant oil and pure diesel fuel for different engine load settings are shown in Figure 1.

There are several clear findings to be drawn from the data presented in figure 1(a) to (c). Firstly, the results indicate that the engine torque, brake power, and specific fuel consumption recorded for D100 and BPO for operation condition (compression ratio 16:1) compares favourably well. The data in figure 1(a) shows a steady increase in engine torque for both D100 and BPO with increase in engine load between 30 and 60%. However within the same operating window, BPO recoded relatively high engine torque compared with D100. However, it is clear from the data presented in figure 1(a) that as the engine load increase from 60% the data recorded for D100 shows a steady increase in engine torque while the data for BPO shows a slight decrease with increase in engine load.

The results in figures 1(b) and (c) also demonstrate that the data recorded for BPO compares favourably well with that for D100. The maximum variation in brake power of 0.63W was recorded at 90% engine load, while the minimum variation of 0.06W was recorded at 60% of engine load, with D100 recording 5.06W. The trends shown in figure 1(b) suggests that the optimum compression ignition engine performance using birrea plant oil occurs at 60% engine load. The data shown in figure 1(c) reinforces this observation, which shows the specific fuel consumption recorded for D100 and BPO. One of the most discernible trends connected to figure 1(c) is that the variations in specific fuel consumption recorded for D100 and BPO between 30% and 60% do not show any significant difference for the fuels under review. The minimum variation of specific fuel consumption between 30% and 60% engine load is 0.01g/kWh, while a maximum of 0.17g/kWh was recorded at the engine load of 90%. Overall, the results in figure 1 indicate that birrea plant oil is a potential fuel. The relationship between fatty acid profile and engine performance analysis results of birrea plant oil indicates potential of converting the same plant oil into quality biodiesel.

IV. Conclusions

An experimental study to examine the profile of free fatty acids found in birrea plant oil and compared against those found in the reference sample has been described. The study also carried comparative tests using B100 and D100 to assess the engine performance. From the experimental results, it can now be concluded that.

a) Birrea plant oil has properties that can enable it to function as a biofuel in IC diesel engines. This implies that transesterifying birrea plant oil under standard conditions may produce biodiesel of international biodiesel quality standards.
b) Trans-Oleic acid is the major fatty acid in birrea pant oil and is not found in reference sample prepared by AccuStandard. This suggests that further investigations on the compositionsition of the same fatty acid need to be carried out. The second most abundant free fatty acid detected was Ethyl Oleate which is an ethyl ester. Other free fatty acids detected are Oleic acid, 3-hydroxypropyl ester, Palmitic acid (methyl ester), Palmitic acid (ethyl ester), suggesting that the oil has strong characteristics required for biodiesel feedstock.
c) The results prove that the performance of IC diesel engine using birrea plant oil is close to pure diesel fuel suggesting that such oil is a potential indigenous feedstock for biodiesel production in Botswana.

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Tables

Table 1 : Fatty acid composition for common oils (% by weight)

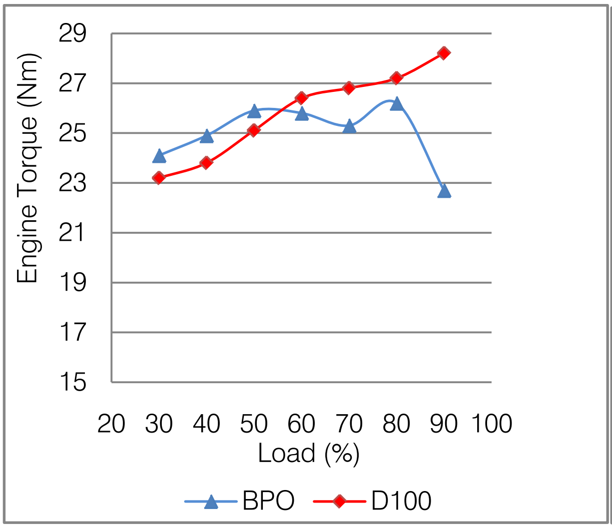
	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid
Number of carbons	16	18	18	18	18
Number of double bonds	0	0	1	2	3
Soybean	8	4	25	55	8
Canola	4	2	60	22	12
Olive oil	10	2	78	10	Trace
Palm oil	44	5	40	10	Trace
Rapeseed oil	3	1	13	14	10
Mustard oil	4	2	24	21	10

Source: Misra, 2010.

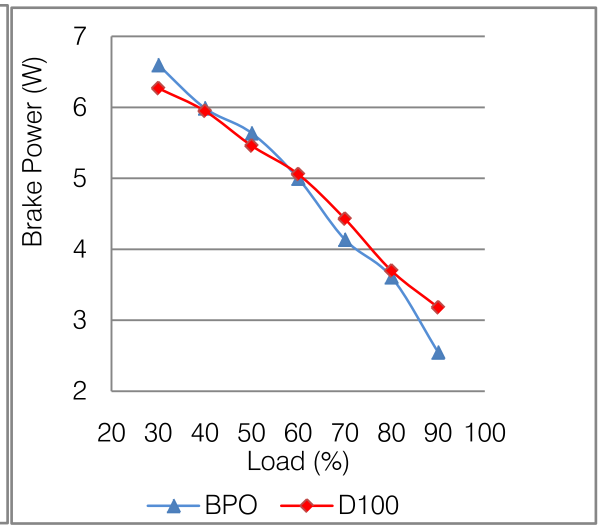
Table 2 : Birrea plant oil fatty acid profile

No.	Fatty acid detected	Status (in standard mixture)	Concentration (mg m^{-3})
1	Palmitic acid	No	-
2	Palmitic acid (ethyl ester)	Yes	115
3	Palmitic acid (methyl ester)	Yes	17.4
4	12-Octadecanoic acid	No	-
5	Trans-Oleic acid	No	-
6	Stearic acid	No	-
7	Ethyl Oleate (Ethyl ester)	Yes	223.5
8	Oleic acid, 3-hydroxypropyl ester	No	-
9	Olein, 2-mono	No	-
10	Olein, 1-mono	No	-

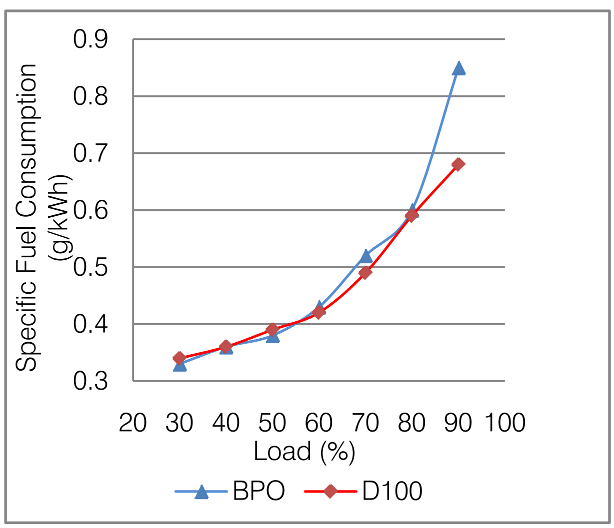
Figures



(a) Engine Torque (Nm)



(b) Brake power (W)



(c) Specific fuel consumption (g/kWh)

Legend: BPO = Birrea plant oil; D100 = 100% Petrodiesel

Figure 1 : Typical engine performance for birrea plant oil and petrodiesel fuel for different engine load settings.