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Sclerocarya Birrea Biodiesel as an Alternative Fuel for Compression Ignition Engines

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Additional information is available at the end of the chapter

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1. Introduction

The continued escalation of fuel prices and environmental concerns among other factors has stimulated active research interest in non petroleum, renewable, and less polluting fuels. Biodiesel (Fatty acid methyl ester) has been identified as a suitable replacement for petroleum diesel in diesel engines [1]. Many feedstocks for biodiesel production have been proposed, with most vegetable oils being suitable substrates. As such, availability of property data is necessary for as many biodiesel fuels as possible, based on different plant oils, to evaluate suitability for use in diesel engines. With birrea plant's huge abundance in Southern Africa and its high kernel oil content [2, 3], property data of its derived biodiesel is deemed necessary. Moreover, one way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils and by products of refinery processes [4]. This study investigated selected properties of birrea biodiesel including chemical composition, viscosity, acidity and calorific value. Engine performance in terms of fuel consumption, brake power and torque at a compression ratio of 16:1, and emission levels of hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen and oxygen were also studied. Petroleum diesel is used to generate similar sets of data in order to compare the performance of the diesel engine using the two diesel fuels. This study is deemed significant as authors are not aware of any study that attempts to investigate sclerocarya birrea plant oil as a potential substrate for biodiesel production. As such, results from this work, including chemical composition, thermo-physical properties and performance of birrea biodiesel, provide new knowledge of a novel fuel source, and provide baseline information for further exploration.

The suitability of biodiesel as a fuel depends on its chemical composition, particularly the length of carbon chain and the degree of saturation of fatty acid molecules. Saturated fat-



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ty acid compounds do not contain double bonds as they contain maximum number of hydrogen atoms that a carbon molecule can hold. From his study on effects of chemical structure on fuel properties, Knothe [5] notes that the presence of double bonds in the fatty acid chains has a significant effect on the properties of the methyl esters. The author further alludes that 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. The authors further echoed that biodiesel produced from such oils may gel at relatively high temperatures [6]. El Diwani et al., [7] reports that carbon-carbon double bonds in unsaturated oils and fats are prone to oxidation by oxygen in the air. The authors further note that 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. Saturated fatty acids are not subject to this type of oxidative attack. Based on all these, it is appropriated to conclude that the choice of oil feedstock determines the resulting biodiesel's position in the trade-off between cold flow properties and oxidative stability. Refaat [8] notes that biodiesel from more saturated feedstock will have higher cetane numbers (thus shorter ignition delay) and better oxidative stability, but will have poor cold flow properties. The author further echoed that biodiesel from oils with low levels of saturated fatty acids will have better cold flow properties, but lower cetane number and oxidative stability.

Several researchers have shown that the physical properties of density, viscosity, and isothermal compressibility strongly affect injection timing, injection rate and spray characteristics [9]. The physicochemical properties of a fuel influence the overall performance of the diesel engine. Viscosity is one of the most important properties of fuels used in diesel engines. It is a measure of the internal fluid friction of fuel to flow which tends to oppose any dynamic change in the fluid motion, and is the major reason why straight vegetable oils are transesterified to methyl esters (or biodiesel). This property influences the injector lubrication, atomization and combustion processes that take place in the diesel engine, and the flow properties. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakages past the piston in the injection pump. If the viscosity is low, the leakage will correspond to a power loss for the engine and if the viscosity is high the injection pump will be unable to supply sufficient fuel to fill the pumping chamber, and again this effect will be a loss in engine power [10]. In a study to analyse performance and emissions of cotton seed oil methyl ester in a diesel engine, Aydin et al. [11] concluded that higher viscosity of biodiesel results in power losses as it decreases combustion efficiency due to poor fuel injection atomization. The dependency of viscosity of fuels like diesel fuel, biodiesel or vegetable oils on temperature was found to be satisfactorily described by an Arrhenius-type equation [12] shown by equation 1.

$$\eta = A e^{B/T} \tag{1}$$

Where η is the dynamic viscosity, T is the operating temperature, A and B are correlation constants. Equation (1) is known as the Andrade correlation and is used in petroleum indus-

try to predict the viscosities of liquid fuels. Heating value of a fuel is another important fuel property that quantifies energy released by a fuel for production of work. Biodiesel fuels do not contain aromatics but they contain fatty acids with different levels of unsaturation. Fuels with more unsaturated fatty acids tend to have a slightly lower energy content (on a weight basis) while those with greater saturation tend to have higher energy content [13]. The authors note that brake power and fuel consumption are also dependent on other properties such as density, viscosity and composition of the fuel.

Most investigations on biodiesel fuels for compression ignition engines show that the use of biodiesel results in lower emissions of carbon monoxide (CO) and hydrocarbons (HC) [14]. Masjuki et al. [2] used preheated palm oil to run a Compression Ignition (CI) engine. The authors reported significant improvement in fuel spray profile and atomization characteristics due to a reduction in the viscosity of fuel as a result of 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. [3] also performed experiments on blending vegetable oil with diesel. The authors report higher exhaust gas temperature with very small variations in CO emission levels and relatively low NOx as compared to petroleum diesel. Ravi et al. [15] performed experiments on a single cylinder slow speed diesel engine operated with soybean biodiesel. The authors concluded that when operated on soybean biodiesel, the engine exhibits higher brake thermal and mechanical efficiencies at all the loads and slightly lower brake specific fuel consumption than when operated on petroleum diesel. In an experimental study to investigate the effects of vegetable oil methyl ester on direct ignition diesel engine performance characteristics and pollutant emissions, Lin et al. [16] found that palm kernel oil methyl ester and palm oil methyl ester, have significantly higher brake specific fuel consumption than most vegetable oil methyl esters fuels due to low volumetric calorific values and shorter carbon-chains. The relative low heating value, high density and high viscosity play primary role in engine fuel consumption for the biodiesel. Reves et al. [17] studied emissions and power of a diesel engine fueled with crude and refined biodiesel from salmon oil; and Ozsezen et al. [18] performed engine performance and combustion characteristics analysis using a direct ignition diesel engine fueled with waste palm oil and canola oil methyl esters. Both studies overally concluded that brake specific fuel consumption is relatively high with biodiesel than with petroleum diesel fuel. Most authors who agree that fuel consumption for biodiesel is relatively high when compared to petroleum diesel attributed it to the loss in heating value of biodiesel.

Some of the key properties of biodiesel derived from selected plant oil species are presented in table 1. Feedstocks for biodiesel production vary with location according to climate and availability, and the most abundant in a particular region are targeted for this purpose. For example, rapeseed and sunflower oils are largely used in Europe for biodiesel production, palm oil predominates in tropical countries, and soybean oil is most common in the USA [19]. The International Grains Council [20] indicated that rapeseed oil was the predominant feedstock for worldwide biodiesel production in 2007, contributing 48% of total production, soybean (22%) and palm (11%). The rest (19%) was distributed among other unspecified vegetable oils and animal fats.

Property	Soybean	Jatropha Curcas	Sunflower	Rapeseed	Reference
Density (kg/m ³), 30°C	¹ 885	² 620, ³ 879	⁴ 860, ⁵ 882	⁶ 877, ⁷ 884	¹ [15]; ² [21]; ³ [22]; ⁴ [23]; ^{5,6} [24]; ⁷ [25].
Calorific Value (MJ/kg)	¹ 37.4	² 41.0, ³ 38.5	⁴ 39.7	⁵ 40.4	¹ [15]; ² [21]; ³ [22]; ^{4,5} [24].
Viscosity (mm²/s), 40ºC	¹ 4.5	² 5.3, ³ 4.8	⁴ 4.719, ⁵ 4.24	⁶ 5.18, ⁷ 6.1	¹ [15]; ² [21]; ³ [22]; ⁴ [23]; ^{5,6} [24], ⁷ [25].
Flash Point (ºC)	¹ 155	² 191	³ 183	⁴ 163	¹ [15]; ² [22]; ³ [23]; ⁴ [25].
Pour Point (°C)	¹ -6	² 3	³ -5	⁴ -15, ⁵ -6	¹ [15]; ² [22]; ³ [23]; ⁴ [24]; ⁵ [25].

Table 1. Properties of biodiesel fuels from selected plant oil feed stocks

This work evaluated chemical properties and engine performance of birrea biodiesel to assess its suitability for use as fuel in diesel engines.

2. Sclerocarya birrea tree

Birrea tree, commonly called marula tree, is indigenous to most parts of Southern Africa. In Botswana, for example, it is widely distributed over the entire country but concentrated in the north eastern part of the country, approximately 250 km north east of Gaborone, Botswana's capital city. The patterns of abundance and distribution can be used to help infer key demographic stages or ecological variables that merit special focus when implementing a management scheme [26]. At maturity, the tree can grow up to approximately 10m to 18m tall with a sterm diameter of approximately 0.8 m on average. The tree grows in warm and dry climatic conditions and is single stemmed with a dense spreading crown and deciduous foliage. It has a thick, relatively short taproot reaching depths of approximately 2.4 m, with lateral roots branching at the upper 0.6m of soil. It bears fruits in clusters of up to three (3) at the end of the twigs (Figure 1(a)). The fruits are round or oval in shape with a diameter of approximately 2.5 to 5.0 cm, and turn pale yellow when ripe [27, 28]. The fruit consists of a hard woody seed covered by pulp and juice which makes the fleshy part of the fruit. It has a delicate nutty flavour and contains a high concentration of vitamin C. The hard seed contains mostly two oil rich nuts (kernel).

There is now a worldwide trend to explore wild plants for oil to augment the already explored sources of feedstock oil for biodiesel production. The fact that the birrea tree grows in drier areas where common oil seeds cannot thrive has stirred interest in it as a valuable source of biodiesel feedstock. Moreover, birrea seeds are normally discarded as by-products of processes that mostly produce birrea juice, wine and snacks from the fruit pulp. Figure 1(b) shows typical snacks produced using birrea fruit pulp.

Though birrea seed kernel is edible, its use as biodiesel feedstock is therefore deemed as utilisation of a relegated resource (birrea seed), and management of by-product.



Figure 1. a): Sclerocarya birrea fruits (b): Typical snacks produced from birrea fruit pulp

3. Materials and methods

3.1. Extraction of birrea kernel oil

Solvent extraction was done to establish true oil content of birrea nuts grown under natural conditions. The process involved seed grinding, soxhlet extraction, filtration, distillation and purging. 200 g of birrea nuts were ground into powder using a mini grinding machine. The powder was then used in the solvent extraction process. The solvent was prepared by mixing 300 ml of hexane and 100 ml of iso-propyl alcohol in a 500 ml flask. The mixture ensures total extraction of all lipids as hexane extracts all non-polar lipids and iso-propyl alcohol polar lipids. Then 3 g of anti-bumping stones (boiling stones) were added to the mixture to ensure non-violent boiling of the solvent during oil extraction. In addition, 75 g of powdered sample was charged into a thimble and placed inside a soxhlet. A soxhlet cover, condenser and heating mantle were then mounted to complete the soxhlet solvent extraction set-up. The solvent was heated until boiling and maintained in that phase for the entire extraction process, which took about 6 hours. After 5 syphones, the extracted liquid became clear, suggesting that there was no more oil in the sample. The process was stopped and the oil rich solvent was allowed to cool to room temperature. Filtration process was then performed to eliminate any possibility of solid particles in the oil rich solvent. The separation of solvent from the oil was achieved through a distillation process performed using a rotary evaporator. The heating bath of the rotavapor used distilled water maintained at approximately 40°C. The condenser used water that is slightly above freezing temperature and was maintained at that temperature using ice blocks. This process should ideally extract all the solvent, starting with hexane (boiling point of 40–60°C) and then iso-propyl alcohol (due to the double bond). However, to ensure that no trace of solvent remains in the oil sample, the oil was purged with nitrogen gas (nitrogen drying) for approximately 40 minutes. Nitrogen is used because it is inert and does not react with oil components.

To ensure that properties of the oil are not distorted, mechanical extraction was done to yield crude oil for subsequent analyses. The mechanism for the extractor consists mainly of a piston, a multi-perforated cylindrical stainless steel compression chamber of approximate-ly 0.15m diameter and 0.3m high, and a hydraulic jack system. The schematic diagram of the mechanism is shown in Figure 2.



Figure 2. Schematic of mechanical oil extraction mechanism

Eight kilograms (8kg) of birrea nuts were charged into a multi-perforated stainless steel compression chamber, with stainless steel discs placed at intervals of 2kg of birrea nuts. The piston was located to keep the top disc into position. The hydraulic system was then operated manually to lift up the platform upon which the multi-perforated stainless steel compression chamber sits, thereby compressing the seeds and forcing the oil out of the kernel and through the 1mm diameter perforations of the compression chamber. The hydraulic system was operated to a maximum pressure of 30 bars to ensure maximum oil extraction while

avoiding over loading the system. The extracted oil was bottled and kept in a cooler box with ice gel pending conversion to biodiesel as described in Section 3.2.

3.2. Birrea biodiesel preparation

Birrea biodiesel was produced through an alkali catalyzed transesterfication process in the laboratory under strict observation and controlled conditions. Alkaline transesterification was preferred since the oil sample had free fatty acid content below 2% [29]. One litre of crude birrea plant oil was filtered, pre-heated to approximately 105°C to eliminate water. The oil was allowed to cool to approximately 58°C and then charged to a 2 litre transparent reaction vessel. A solution of methanol of 99.5% purity and 7.5g of potassium hydroxide pellets of 98% purity as catalyst was prepared and charged to the reaction vessel. The molar ratio of methanol to oil was fixed at 1:6, which is optimal ratio for the transesterification of vegetable oils [23]. The reaction vessel was tightly closed and contents agitated using a mechanical shaker for one hour. The reaction vessel was then set up-side down and allowed to cool for a further 3 hours. Two distinct layers were formed, the upper layer being the methyl ester and the lower layer was glycerol (due to its higher specific gravity). Glycerol was drained off from the bottom of the reaction vessel until only biodiesel (and possibly traces of unreacted methanol) remained. The biodiesel was then water washed twice with distilled water to ensure removal of all traces of glycerol. A rotary vacuum evaporator was used to recover the unreacted alcohol from the biodiesel.

The petroleum diesel used for comparison was purchased from a Shell petrol Station and had properties including boiling point of 422 K, vapour pressure of 53 Pa, density of 871Kg m⁻³, viscosity of 2.3 mm²/s at 40^oC, acidity of 0.2 mgKOH/g, calorific value of 50.4 MJ/Kg and cetane number of 48.

3.3. Chemical analysis

Chemical analysis was done to identify esters present in the birrea biodiesel sample. The method involved analysing standard (reference) samples, generating calibration curves for esters identified in the standard samples, and identifying and quantifying esters present in the birrea biodiesel sample.

To establish the chemical composition of the standard samples, Methyl Arachidate was injected into the standard mixtures as an internal standard (IS) and the samples were run ten (10) times through the Gas Chromatograph - Mass Spectrometry (GC-MS) system at ten (10) concentrations of equal interval from 10ppm (parts per million) to 1ppm. At each concentration, peak areas and retention times for all esters present were captured from the chromatogram. Peak area ratios (Analyte/IS) were calculated for all esters present at all concentrations, and these were used to generate calibration curves for each ester in the standard samples. The birrea biodiesel sample was also run through the GC-MS system under similar conditions. Peak area ratios (Analyte/IS) were calculated for each ester detected in the biodiesel sample and ester concentration was then determined by interpolation from a calibration curve of corresponding compounds. The instrument used for composition analysis is the Waters GCT premier Time of Flight (TOF) mass spectrometer (MS) coupled to the Agilent 6890N gas chromatograph (GC) system. In addition, the National Institute for Standards and Technology (NIST) developed Automated Mass Spectral Deconvolution and Identification System (AMDIS) software package, (chemdata.nist.gov/massspc/amdis) was used for peak identification. The Automated Mass Spectral Deconvolution and Identification System 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.

3.3.1. Gas chromatograph conditions

One micro litre (1 μ l) of birrea biodiesel sample extract was injected into the system using an auto-injector. The injector temperature was set at 260°C 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°C for 2 minutes, and then gradually increased from 100°C to 290°C at a rate of 10°C per minute. The total run time was approximately 35 minutes.

3.3.2. Mass spectrometer conditions

The mass spectrometer (MS) conditions that were employed were a positive polarity of electron ionisation (EI), a source temperature of 180° C, and an emission current of 359μ A. Other MS conditions including electron energy and resolution were set by the system's auto tune function. Detection was by the micro channel plate detector (MCP) whose voltage was set at 2700 V. The sample 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.

3.4. Viscosity analysis

Birrea biodiesel and petroleum diesel were analyzed using a Fungilab Premium Series (PREL 401024) viscometer coupled to a Thermo Fisher Scientific heating bath circulator. The heating bath circulator was three-quarter (³/₄) filled with distilled water. 3ml of both fuel samples were weighed in order to determine their densities. The viscometer was setup with the appropriate spindle and heating jacket. The LCP (low centipoise) spindle was selected for these experiments since low viscosity fluids were analyzed. The spindle was connected and the machine calibrated with the density of the fluid to be tested and the appropriate speed for the spindle. After appropriately assembling the apparatus, the sample to be tested was added in such a way that the spindle was completely submerged. The instrument was then run, with the heating bath turned on and set to 95°C. The spindle speed (RPM) could be varied based on the torque values, with the ideal range being 60-95%. Sample viscosity readings were then recorded at temperature intervals of 5°C from room temperature to 60°C as hot water was circulating between the heating bath and the heating jacket of the viscometer. The Data logger application software was used to download to a personal computer the experiment data from the viscometer for storage and analysis.

3.5. Acid value determination

Acid value measurements of diesel sample extracts were carried out by titration technique according to ASTM D664 standard test method [30]. Based on the same standard 125 ml of solvent, consisting of 50% isopropyl alcohol and 50% toluene was prepared in a 600 ml beaker. 5 g of sample was then added to the beaker, followed by 2 ml of phenolphthalein indicator. The solutions were titrated with 0.1M KOH to the first permanent pink colour. Three titrations were carried out for each of the four sample extracts and the average titration values determined. The acid values were determined using equation 2 and percentage of free fatty acids using equation 3.

Acid value,
$$AV = \frac{56.1 \times N}{W} \times Average \ Titration \ Value$$
 (2)

Where, 56.1 = molecular weight of KOH

N = molarity of the base

W = weight of sample in grams

Free Fatty Acids (%)=
$$0.5 \times AV$$
 (3)

3.6. Energy content

The calorific values of birrea biodiesel and petroleum diesel (for comparison purposes) samples were determined using the IKA C200 Calorimeter system whose main components include the basic device, decomposition vessel, ignition adapter, combustion crucible and oxygen filling point. The system has automatic data acquisition through the CalWin calorimeter software which handles calculations for the calorific values of samples.

3.6.1. Calorimeter conditions

To determine the heating values of samples, 3ml of sample extract were weighed and placed in a combustion crucible at a temperature of approximately 22. The crucible was then closed up inside a decomposition vessel, which in turn was filled with oxygen at a pressure of 30 bars for 30 seconds to ensure adequate oxygen for combustion processes. The cooling water in the tank fillers was kept at initial temperature of within 18°C – 24°C range. The oxygenfilled decomposition vessel was inserted into the measuring cell that is equipped with a magnetic stirrer. The cell cover was then closed for the test to commence. Total run time for each experiment was 8.2 minutes.

3.7. 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 as demonstrated by figure 3. The dynamometer was used for engine loading. 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. The layout of the experimental setup is shown in Fig. 3, while engine specifications are presented in Table 2.



Figure 3. Schematic diagram of the experimental setup.

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. Prior to the data recording, the compression ratio was set to the desired level and the engine speed was set to a maximum of 2500 revs/minute at full throttle. The engine was allowed to run on petroleum diesel fuel under steady state operating conditions, as opposed to transient conditions characterised by the stop-go type of pattern, for approximately 30 minutes to reach fully warm conditions. This ensures best engine efficiency and effective burning of effects of the warm up cycle and to clear out any moisture from the system and exhaust. This also established the engine's operating parameters which constitute the baseline that was compared with the subsequent case when the birrea biodiesel was used. After the engine operating temperature had stabilised, the first sets of readings for brake power, engine torque and specific fuel consumption at the maximum speed of 2500 revs/min were recorded. The dynamometer load was then increased by adjusting the load current control mechanism until the engine speed reduced by steps of 250 revs/min to a minimum value of 1000 rpm. For each step, the data for brake power, engine torque and specific fuel consumption were automatically captured onto a PC using the data acquisition software provided by the engine manufacturer. All measurements were repeated three times for each test setting, while the test sequences were repeated three times.

Parameter	Specification
Make	Farymann
Туре	A30
Compression ratio	Variable 5:1 to 11:1(Petrol), 12:1 to 18:1(Diesel)
Number of cylinders	1
Cylinder bore	95 mm
Stroke	82 mm
Swept volume	582 cc
Speed range	1000 to 2500 rpm (2750rpm overspeed cut-out)
Max Power	9.5kW
Max torque	45Nm
Ignition timing	30° BTDC to 10° ATDC
Choke sizes	19, 21, 23, 25mm
Dynamometer d.c motor	5-7kW 2500 rpm with thermostat

Legend. BTDC: Before Top Dead Centre; ATDC: After Top Dead Centre. Source: [31]

Table 2. Engine Specifications

3.8. Emissions measurement

Emissions measurement was carried out using an EMS Exhaust Gas Analyzer (EMS 5002-W&800) that works on the EMS exhaust gas analyzer system software and the Driveability and Emissions Calculation Software (DECS). At the commencement of engine performance analysis described in section 2.7, the Exhaust Gas Analyzer was powered, allowed to warm-up for 10 minutes, and to zero (setting all the gases to zero). The sample hose was then connected, with the probe placed in the tail (exhaust) pipe. Readings were taken at intervals of 250 rpm of engine speed after conditions had stabilised at each speed. The technology of this analyzer allows for auto calibration before every analysis and a high degree of accuracy in the analysis of low concentrations of gases found in the engine. The DECS software was used for calculating and analysing other emissions related engine performance characteristics. For purposes of repeatability, the emission analyser accuracy and measuring range are shown in Table 3.

Parameter	Accuracy	Range
Hydrocarbons (HC)	4.00 ppm	0 – 24 000 ppm
Carbon monoxide (CO)	0.06%	0 - 10%
Carbon dioxide (CO ₂)	0.30%	0-20%
Oxygen (O ₂)	0.10%	0-25%
Nitrogen oxides (NO _x)	1.00 ppm	0 – 5 000ppm

Table 3. Emissions analyser accuracy and measuring range.

4. Results and discussion

4.1. Birrea seed oil yield

The oil yield of birrea seeds regarded as the actual oil content in this study is the one determined using solvent extraction method and not mechanically extracted, as the latter is dependent on machine efficiency. After running four soxhlet extractions, the average oil content of birrea seeds was determined to be 58.56% by mass. Table 4 compares oil yield level of birrea seeds with that of mostly studied plant species obtained from literature.

Plant species	Yield (%Weight)	References
Sclerocarya birrea	58.56	
Jatropha curcas	¹ 63.16; ² 46.27; ³ 50-60	¹ [32]; ² [33]; ³ [21]
Linseed	¹ 33.33	1[34]
Soybean	¹ 18.35; ² 20.00	¹ [34]; ² [35]
Palm	144.60	1[34]

Table 4. Oil yield levels of birrea seeds and common oil seed species.

4.2. Birrea biodiesel chemical composition

The chemical composition of birrea biodiesel was analysed according to the procedure described in section 2.3. Standard (Reference) samples supplied by AccuStandards were analyzed to confirm that sample composition matched the composition listed on technical data sheets that accompanied the samples. To draw calibration curves for each ester identified in the standard samples, peak area ratios (Analyte/IS) were plotted against actual ester concentration in parts per million (ppm) for different gross concentrations of standard samples. Actual concentration of an ester was calculated as a percentage of the same ester's concentration (as per standard sample data sheets) multiplied by gross concentration of the standard sample at varying dilution levels. Figure 4 shows a typical calibration curve for methyl palmitate for the standard sample.

To quantify the methyl palmitate detected in birrea biodiesel, the peak area ratio of the ester (Analyte/IS) was calculated and used in the calibration curve above to interpolate the actual concentration of the compound. The concentration value was validated by substituting the peak area ratio value for the y-value in the equation of the straight line graph and calculating the value of x, which represents the concentration of Methyl palmitate in birrea biodiesel. The R² value, also called the goodness of fit, is a correlation value which indicates how closely a function fits a given set of experimental data.



Figure 4. Methyl palmitate calibration curve for the standard sample

The composition analysis of birrea biodiesel was done using a combination of AMDIS (Automated Mass Spectral Deconvolution and Identification Software) and Data Analysis Software at a minimum match factor of 70%. The total number of compounds identified is forty-five (45), of which thirty-six (36) are esters (appendix 1). The peak areas of the compounds were used to establish the ester content of the biodiesel sample. Using analysis data shown in appendix 1, ester content was computed to be 82% according to equation 4. This is about 15% below the requirements of the European standard EN 14214. The American Standard, ASTM D 6751-02, has no specification for this property. The ester content may however be improved by modifying the biodiesel conversion process as discussed in section 3.3.

Ester content
$$\binom{\%}{=} \frac{\sum (\text{Peak areas of all esters})}{\sum (\text{Peak areas of all compounds})} \times 100$$
 (4)

Some of the most abundant esters identified in birrea biodiesel are presented in table 5, together with their concentrations, while the complete list of constituent compounds is appended.

Compound	Concentration (µg/ml)
Methyl palmitate (C16:0)	1993.71
Methyl Oleate (C18:1)	2294.72
Methyl Stearate (C18:0)	1044.37
Methyl Linoleate (C18:2)	560.18

Table 5. Ester composition of birrea biodiesel

The ester composition of birrea biodiesel indicates that the most abundant compounds include methyl palmitate, methyl oleate, methyl stearate and methyl linoleate. These are all long chain compounds that are largely saturated, with a small degree of unsaturation. The characteristic ester composition of birrea biodiesel depicted by the mixture of these compounds has a strong influence on its fuel properties. Fuel properties of plant oil and its derived biodiesel improve in quality with increase in carbon chain length and decrease as the number of double bonds increase, except for cold flow properties as mentioned in section 1. Thus the cetane number, heat and quality of combustion, freezing temperature, viscosity and oxidative stability increase as the chain length increases and decrease as the number of double bonds increase. A fuel whose constituent mixture of compounds is fully saturated will depict higher cetane number and better oxidative stability, but poor cold flow properties. The small degree of unsaturation depicted by the presence of double bonds in compounds like Methyl Oleate and Methyl Linoleate is significant as double bonds inhibit crystallization, thus lowering the cloud point of the fuel. A low cloud point is a desirable fuel property as it ensures that a fuel remains in the liquid phase at low temperatures. Thus birrea biodiesel has a good properties trade-off between cold flow properties, oxidative stability and cetane number. The viscosity analysis profile of birrea biodiesel is presented in section 4.3.

4.3. Viscosity analysis of birrea biodiesel and petroleum diesel fuels

It is integral to evaluate the viscosities of fuels in order to determine the feasibility of use in a diesel engine since viscosity influences fuel atomization and the combustion process. The viscosity profiles of birrea biodiesel and petroleum diesel fuels were analysed. Figure 5 shows profiles of viscosity variation with temperature for the two diesel fuels, with each data point representing an average of three viscosity measurements. Viscosity limits for the American standard testing methods (ASTM-D6751) and the European standards (EN 14214) are also included in the same figure for quick assessment of conformance to major international biodiesel quality standards.



Figure 5. Viscosity variation with temperature

From figure 5, it is evident that birrea biodiesel largely meets quality requirements of both ASTM D-6751 and EN 14214 standards, while petroleum diesel (used in this study) viscosity profile is significantly lower than the requirements of the European standards. The kinematic viscosity at 40°C indicates that birrea biodiesel has better lubricity than petroleum diesel and is likely to have a better combustion profile when used as a fuel in a diesel engine. The low viscosity of petroleum diesel may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in increased wear or leakage. Leakage will, under normal circumstances, correspond to a power loss for the engine as mentioned earlier. The birrea biodiesel fuel was therefore found to be suitable for use in compression ignition (CI) engine.

4.4. Acidity of birrea biodiesel fuel

Analytical tests were conducted in a study to establish acidity levels of birrea biodiesel and petroleum diesel fuels. The experimental data were recorded as described in section 3.5. After running five titrations on birrea biodiesel sample, computation of the mean revealed an acid value of 0.62 mgKOH/g and a free fatty acid value of 0.31%. The acidity of birrea biodiesel fuel closely compares with that of petroleum diesel (section 3.2).

These results indicate that the level of acidity of birrea biodiesel meets specifications of ASTM D 664 (0.8 mgKOH/g maximum), and is marginally out of specifications of EN 14214 biodiesel standard (0.5 mgKOH/g maximum). Acid value is a direct measure of free fatty acids (FFAs) in the biodiesel. Free fatty acids are undesirable in the fuel because they may cause corrosion of the fuel tank and engine components. The free fatty acids in the biodiesel could be reduced by neutralising birrea parent oil with an alkaline solution prior to transesterification, and two-stage processing, for example, acid esterification followed by alkaline

transesterification [36, 19]. The overall quality of birrea biodiesel is however deemed acceptable as it meets ASTM specifications.

4.5. Heat of combustion

Heat of combustion is the thermal energy that is liberated upon combustion, and is commonly referred to as energy content. A systematic study was conducted to analyse energy content levels of birrea biodiesel and petroleum diesel fuels. The experimental data were recorded as described in section 3.6. After running four experiments for each of birrea biodiesel and petroleum diesel fuel samples, computation of mean values revealed calorific values of 42.4 MJ/kg and 50.4 MJ/kg for birrea biodiesel and petroleum diesel fuels respectively. Unlike petroleum diesel, biodiesel fuels do not contain aromatics but fatty acids with different levels of saturation, and energy content decreases with increase in the degree of unsaturation [13]. Thus the lower energy content of birrea biodiesel relative to petroleum diesel fuel is to be expected. However, energy content of 42.4 MJ/kg for birrea biodiesel fuel compares favourably well with biodiesel fuels from other feed stocks. Ravi et al. [15] found that the gross heat of combustion for soybean biodiesel is 37.4 MJ/kg, while that of jatropha curcas was found to be 41.0 MJ/kg [21].

4.6. Engine performance analysis

The performance of the variable compression ignition engine was evaluated in terms of specific fuel consumption, engine torque and engine brake power. Some of the key properties of birrea biodiesel fuel used in this study are summarised in table 6.

Property	Value	ASTM D-6751	EN 14214
Density (kg/m³)	973	-	860 - 900
Viscosity, 40ºC (mm²/s)	3.95	1.9 - 6.0	3.5 - 5.0
Acidity (mgKOH/g)	0.62	0.8 max	0.5 max
Free Fatty Acids (%)	0.31	(\Box / O)	
Calorific values (MJ/kg)	42.4	-	

Table 6. Properties of birrea biodiesel fuel

Performance tests were conducted for compression ratios 14:1 through 18:1, but to enable the main findings of the study to be identified clearly, only performance results for compression ratio 16:1 are presented and discussed. The results for birrea biodiesel were compared with results for petroleum diesel fuel, whose properties are presented in section 3.2. The experimental data were collected as discussed in Section 2.5; leading to results presented in figure 6(a) to (c).

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Figure 6. Variation of engine performance for birrea biodiesel and petroleum diesel fuels with engine load. *Legend: Birrea B100 = 100% Birrea biodiesel.*

There are several clear findings to be drawn from the data profiles presented in figure 6. Generally, the results clearly indicate that birrea biodiesel performs significantly better than petroleum diesel in terms of fuel consumption, engine torque and engine brake power. This is contrary to general knowledge from most research outputs that rank the performance of biodiesel fuels lower than that of petroleum diesel [17, 18]. This may partly be due to the higher thermal efficiency of birrea biodiesel when compared to fossil diesel as shown in table 7. The improved thermal efficiency of biodiesel is attributed to the oxygen content and higher cetane number.

The fuel consumption profiles shown in figure 6(a) indicate that birrea biodiesel performs better than petroleum diesel across all engine loads under review. The maximum variation between the two fuels is 48% at engine load of 90%, and the minimum variation is 34% at engine load of 30%. The variation of specific fuel consumption also depicts birrea biodiesel to be a more economic fuel for the diesel engine than petroleum diesel. The changes in specific fuel consumption and power depend on engine design, speed and loading conditions. Engines with higher compression ratios would result in higher temperatures and pressures during combustion in the cylinder, promoting more complete combustion. Engine speed also affects the airfuel mixing process, with higher engine speed normally giving a better mixture and higher cylinder temperature and pressure. On the contrary lowering the engine speed would lower the cylinder temperature and this can lead to poor vaporization and atomization.

The economic value of birrea biodiesel as a fuel in CI engine is further validated by its remarkably high engine torque shown in figure 6(b). For both petroleum diesel and birrea biodiesel fuels, torque increases steadily to maximum values of 20.1 Nm and 27 Nm respectively and then gradually decreases to minimum values of 10 Nm and 23.1 Nm respectively at engine load of 90%. The disparity in the generated torque can be attributed to the improved combustion processes caused by increased atomisation and spray characteristics for biodiesel fuel.

The brake power profiles shown in figure 6(c) indicates a gradual decrease with increase in engine load for both diesel fuels, with birrea biodiesel recording relatively high values when compared to petroleum diesel across the entire engine loads under review. This is consistent with the high torque shown in figure 6(b).

Overall, the results in figure 6 indicate that birrea biodiesel is a suitable fuel for the compression ignition engine. A summary of engine performance using birrea biodiesel in comparison with petroleum diesel and jatropha curcas biodiesel fuels at a speed of 2500rpm and engine load of 30% is presented in table 7.

Performance	Sclerocarya Birrea B100	Petroleum diesel	Jatropha curcas B100 [21]
Brake power (W)	6.84	5.00	8.95
Specific fuel consumption (g/kwhr)	0.32	0.43	0.63
Torque (N)	24.9	17.9	-
Fuel flow (kg/hr)	2.16	2.15	0.62
Brake thermal efficiency (%)	67.8	65.5	24.09
Mass of air (kg/hr)	37.25	36.52	5.52
Air fuel ratio	17.25	17.01	8.9

Legend: B100 = 100% biodiesel

Table 7. Engine performance using birrea biodiesel, petroleum diesel and jatropha biodiesel fuels.

The exhaust emissions produced from the engine performance analysis are discussed in Section 4.7.

4.7. Emissions analysis

This section compares emission levels of unburned hydrocarbon (HC), carbon monoxide (CO), and carbon dioxide (CO₂) when the engine under review runs on petroleum diesel and on birrea biodiesel fuel (B100). The experimental data recorded for the three pollutants are presented in figure 7(a), (b), and (c). Typical engine combustion reaction is summarised by equation 5.

Fuel + Air
$$(N_2 + O_2) = CO_2 + CO + H_2O + N_2 + O_2 + HC + O_3 + NO_2$$
 (5)

This section however focuses on HC, CO and CO_2 only. Figure 7(a) shows the data on emission levels of HC recorded when the engine was using petroleum diesel and birrea biodiesel. One of the most discernible trends connected to the data in figure 7(a) is that combustion of birrea biodiesel provides a significant reduction in unburned HC.

The difference in magnitude of HC emissions between the two diesel fuels increases with increase in load in a near exponential relationship. Based on average values, combustion of birrea biodiesel provides a reduction of unburned HC of approximately 59.4% at the compression ratio of 16:1. The lower HC emissions may be attributed to the availability of oxygen and high cetane number in biodiesel, which facilitates better combustion. It is the view of the authors that the relatively low level of HC emissions recorded when the engine was run using birrea biodiesel is linked to the quality of the biodiesel in terms of kinematic viscosity profile which complies favourably well with more stringent international standards such as the European standard (EN 14214), as demonstrated by figure 5.

Figures 7(b) and (c) show variation of CO and CO_2 emission levels respectively with increase in engine load.

The data in figures 7 (b) and (c) should be viewed and discussed in parallel to enable the correlation between CO and CO_2 emission levels to be identified and explained for the operational conditions under review.

Considering the results in figures 7(b) and (c), it can be seen that CO and CO₂ emissions of petroleum diesel tend to increase with increase in engine load, while the same emissions for birrea biodiesel tend to increase gradually with increase in load for low load ratings. However, the data in figure 7(b) show that both diesel fuels recorded the same average value of 1.5% by volume of CO emissions, while figure 7(c) depicts a slightly higher average value of CO_2 for birrea biodiesel. CO is one of the consequences of incomplete fuel combustion. Less CO is generated with biodiesels than diesel for engine load below 60%. Concentration of oxygen during combustion would enhance the oxidation rate of CO and lead to less CO formation. This is a major advantage of oxygenated fuels like biodiesel. However, at higher engine loads, the lower temperatures could hinder the conversion rate of CO to CO_2 , leading to higher CO emissions. These effects are mainly attributed to the complex interactions between combustion dynamics and physicochemical properties of the fuel. The combustion ef-

ficiency depends on the engine design, injection system, air-fuel mixture, and the loading and speed conditions. The physicochemical properties of birrea biodiesel may be affected by feedstock variations, conversion process and separation efficiency. Factors such as chemical compositions, carbon-chain lengths, degree of saturation and impurities also influence the performance of the biodiesel as a fuel in the diesel engine.



Figure 7. a): Unburned hydrocarbon (HC) Emissions of the two diesel fuels (b): CO Emissions of petroleum diesel and birrea biodiesel (B100) (c): CO₂ Emissions of petroleum diesel and birrea biodiesel (B100)

Overall results indicate that using birrea biodiesel in a compression ignition engine provides significant reduction in HC emission levels than petroleum diesel, while levels of CO and CO_2 emissions are quite comparable.

5. Economic feasibility of using Sclerocarya birrea to produce biodiesel

The future outlook of the Sclerocarya birrea biodiesel fuel is bright on the basis of abundance and minimal conflict with food security. As discussed in section 2, Sclerocarya birrea plant is abundant in Botswana and an almost negligible fraction is utilised for purposes that use the fruit pulp and juice, discarding the seed as a byproduct. Thousands of tons of the fruits are left to rot annually as an untapped resource. The major economic factor to consider with respect to the input costs of biodiesel production is the feedstock, which is about 80% of the total operating cost [37]. Other important costs relate to the geographical area of the feedstock, variability in crop production from season to season, labor and production inputs including methanol and catalyst. These costs depend on the prices of the biomass used and the size and type of the production plant. Other important factors that would determine the production cost of birrea biodiesel are the yield and value of the byproducts of the biodiesel production process, such as oilseed cake (a protein-rich animal feed) and glycerine (used in the production of soap and as a pharmaceutical medium). Since birrea nut oil has not been studied as a potential feedstock for production of biodiesel, precise production costs are yet to be established.

This study aims to establish the technical properties of the biodiesel as a suitable fuel for the compression ignition engine, thereby providing a basis upon which socio economic feasibility analysis can be done to further the research. Factors including actual yield of birrea fruits per hectare and associated production and logistics costs will need investigation.

Production of biodiesel from sclerocarya birrea will however have other obvious social impacts. It will provide a source of income and employment for many families. Thousands of rural people who are largely unemployed would earn income from the gathering and processing of the raw material into biodiesel. Thus the logistics of harvesting the raw material is deemed simple and cost-effective. Furthermore, the fact that sclerocarya birrea tree thrives and produces abundantly under natural (unoptimised) conditions implies a substantial reduction in overall costs of producing biodiesel from this plant species. Optimising growing conditions, if desired, may increase the yield.

Although birrea fruit production is seasonal under natural conditions (follows the rain season), nut availability for oil extraction can be perennial. When the hard woody seed has been extracted from the fruit skin and pulp and allowed to dry, it can stay for more than a year with no damage to the nut in its cavity. Thus there are two options for keeping this raw material inventory. One option is to keep hard seeds and only crack them when oil extraction is about to commence. This eliminates (or largely minimises) inventory holding costs on the delicate seed bearing the oil. The other option is to crack all the seeds and keep in stock the oil bearing nuts, but this requires special preservation facilities which come at a cost.

On the basis of abundance and the results discussed in this chapter, Sclerocarya birrea biodiesel is recommended for production in Botswana.

6. Conclusions

Several conclusions can be made from the experimental work discussed in this chapter. These include the following;

- i. Sclerocarya birrea biodiesel used in this study has an ester content of 82%. This is deemed to be high and can be improved by subjecting the parent oil to a two stage transesterification process.
- **ii.** The viscosity of birrea biodiesel at 40°C meets both the ASTM-D6751 and EN 14214 international quality standards. Its viscosity profile appears to be superior to that of petroleum diesel.
- **iii.** The heating value of birrea biodiesel was found to be 42.4 MJ/kg, thus 8MJ/kg lower than that of petroleum diesel used in this study. It is however on the high side relative to biodiesel fuels derived from most vegetable oils.
- **iv.** The performance of CI diesel engine using birrea biodiesel fuel was surprisingly found to be significantly better than that using petroleum diesel in terms of fuel consumption, engine torque and break power. Specific fuel consumption, for example, has a maximum variation of 48% and a minimum variation of 34% between the two fuels.
- v. The level of HC emissions produced from combustion of birrea biodiesel was remarkably lower than that of petroleum diesel by a magnitude of approximately 59.4% at the compression ratio of 16:1. Emission levels of other exhaust gases produced by the two diesel fuels were largely comparable.
- vi. Overall, birrea biodiesel fuel used in this study was at the least comparable to petroleum diesel in terms of fuel properties and performance, and should be advocated for use in CI diesel engines.

Like any other study, this work was not without limitations. The first limitation regards the effect of weather, soil and plant variations on oil yield and properties. The study was not able to test seed oils from birrea plant specimens from several locations and growing conditions to establish the effect of these factors on oil yield and properties of derived biodiesel.

Furthermore, this study investigated birrea biodiesel processed from crude parent oil that was extracted from plants growing under natural conditions. Since oil yield under natural conditions may differ significantly from that under optimised conditions, the result established in this study serves to provide baseline data for determining indigenous oil plants that are good candidates for further exploration.

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Appendix 1

Chemical composition of sclerocarya birrea biodiesel at 70% match factor.

Peak #	Ret	Area	Compound Name	Compound
reak #	Time	Alea		Туре
1	10.649	89593610	Methyl tetradecanoate	ester
2	10.759	248711863	Tridecanoic acid methyl ester	ester
3	12.297	11762782	1.2-benzenedicarboxylic acid,bis(2-methyl propyl) ester	ester
4	12.561	154502042	9-Hexadecenoic acid, methyl ester	ester
5	12.848	5773983254	Hexadecanoic acid methyl ester	ester
6	12.972	1472336051	decanoic acid methyl ester	ester
7	13.046	1625971299	Pyradazin-3(2H)-one	ketone
8	13.12	1385277087	Pentadecanoic acid methyl ester	ester
9	13.25	4284563596	Heptadecanoic acid methyl ester	ester
10	13.569	31847458	Heneicosanoic acid methyl ester	ester
11	13.838	206216774	Octadecanoic acid methyl ester	ester
12	13.902	94186693	Tetradecanoic acid methyl ester	ester
13	13.97	102294655	Eicosanoic acid methyl ester	ester
14	14.038	278766060	9,12octadecadienoic acid(Z,Z)-methyl ester	ester
15	14.546	1765470999	Isopropyl Linoleate	ester
		/		
16	15.203	769700914	2-Fluorobenzylamine	amine
17	15.25	1604733504	4-Biphenylol 3,3-dinitro	Biphenyl
18	15.337	1731581422	Ethyl oleate	ester
19	15.436	966708117	2-chloroethyl oleate	ester
20	15.494	484782015	9-octadecenoic acid methyl ester	ester
21	15.522	428166076	12-octadecenoic acid methyl ester	ester

Peak #	Ret Time	Area	Compound Name	Compound Type
22	15.565	1657554718	10-octadecenoic acid methyl ester	ester
23	15.655	80871606	Docosanoic acid methyl ester	ester
24	15.7	171812597	Cyclopropaneoctanoic acid methyl ester	ester
25	15.758	291675860	Ethyl 18-nonadecenoate	ester
26	15.86	81633259	5,8,11-Heptadecatrienoic acid methyl ester	ester
27	15.954	95949996	7,10,13-Eicosatrienoic acid methyl ester	ester
28	16.026	95096869	9,12,15-octadecatrienoic acid methyl ester(Z,Z,Z)	ester
29	16.221	159226154	Octadecylamine	amine
30	16.407	1463522225	2,3-Dimethyl-3-heptene,(Z)	alkene
31	16.592	1919891430	Nonadecanoic acid 10-methyl ester	ester
32	16.663	56034037	11,13-Eicosanoic acid methyl ester	ester
33	16.757	146143060	Hexanedioic acid,dioctyl ester	ester
34	17.151	2555750058	Octadecylamide	amide
35	17.267	52761700	Decyl oleate	ester
36	17.637	33199071	13-octadecenoic acid methyl ester	ester
37	17.828	25670426	8-octadecenoic acid methyl ester	ester
38	18.02	540972554	15-Tetracosanoic acid methyl ester	ester
39	18.208	210084471	1,2-Benzenedicarboxylic acid,mono(2-ethylhexyl) ester	ester
40	18.73	72898469	Tricosanoic acid methyl ester	ester
41	18.961	83593780	Phthalic acid,octyl 2-pentyl ester	ester
42	19.083	19809218	squalene	alkene
43	19.49	561590599	Hexatriene	alkene
44	20.177	110377495	3-Ethyl-3-methylheptane	alkane
45	20.945	109244630	Heptacosanoic acid,25- methyl ester	ester

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