Characterizing Sunflower Oil Biodiesel Blends as Alternatives to Fossil Diesel

Daniel M. Madyira, Zanele Nkomo, and Esther T. Akinlabi, Member, IAENG

Abstract—This paper reports on investigation into the feasibility of using sunflower oil based biodiesel blends as alternatives to fossil diesel fuel. The current global reliance on fossil fuels is coming to an end. This is driven on one hand by the dwindling global fossil fuel reserves and the understanding of the consequences of carbon accumulation in the atmosphere on the other. Dwindling reserves continue to drive global fuel prices upwards with negative effects on economic performance. Continued accumulation of carbon dioxide in the atmosphere is perceived to be responsible for the Greenhouse Gas (GHG) effect. This dual problem can be addressed by using alternative renewable fuel sources, which guarantee continued supply while maintaining global carbon neutrality. Biofuels are now largely recognized as viable options. Some of the challenges of using biodiesel in conventional diesel engines are their low density, which leads to low calorific value and acidity levels that threatens the structural integrity of the engine. Blending biodiesel with petroleum diesel can mitigate these effects and lead to better performing fuels. Fuel characterization is therefore essential to establishing notable similarities and differences between biodiesel and fossil diesel, and in determining optimum blending proportions for more effective use of biodiesels. In this investigation, biodiesel was produced from commercial sunflower cooking oil using the batch transesterification process with methanol in the presence of Sodium hydride catalyst. The characterization of the biodiesel was then conducted using Nuclear Magnetic Resonance (NMR), bomb calorimetry, acidity and flash point analysis, sulphur content tests and Gas Chromatography (GC). Blends ranging between 5% and 50% biodiesel concentration in Ultra-Low Sulphur Diesel (ULSD), in increments of 5% were analyzed. Results obtained confirmed that biodiesel has lower calorific value than ULSD, implying higher fuel consumption. The high flash point, almost at a temperature twice as high as that of ULSD, though advantageous for storage and transportation, results in poor ignition. The results also suggest that an increase in concentration of biodiesel leads to larger difference in properties between the blend and the ULSD. The pH value of biodiesel was found to be lower than that of ULSD which compromises engine structural integrity. Biodiesel’s chain length was found to contain an average of 19 carbons which makes it a viable option when compared to ULSD. Despite the relatively inferior properties measured, biodiesel still remains one of the most attractive fuel options.

Index Terms— Biodiesel blends, fossil diesel, sunflower oil

I. INTRODUCTION

The growing concern related to the depletion of natural fossil fuel reserves caused by extensive usage necessitates the search for renewable energy sources and fuels. The depletion of the ozone layer and the consequent global warming related warnings heighten the importance of discovering and developing alternative energy and fuel sources. The current shortage of oil and other fossil fuels threaten not only economic performance, but the state of the environment as well. Over the last 100 years, the atmosphere has seen a doubling of carbon dioxide concentration largely as a result of industrialization and uncontrolled use of fossil fuels for transportation and energy generation [1]. Currently, approximately 80% of the energy consumed worldwide is from fossil sources and 58% of that energy is used for transportation [1]. The most highly used sources of energy throughout the world are crude oil and coal, which are also used to produce various petroleum products. The projected increase of petroleum demand in 2025 is 40% [2]. Furthermore, the energy used by the transportation industry in Europe increased 22% from 1990 to 2000 [3]. This level of energy use requires extensive extraction activities that may not cope with future demand. Therefore, suitable alternatives to fossil fuels in the form of biofuels are being investigated by researchers around the globe. Biofuels, which regained popularity in the 20th century, are fuels obtained from biomass [2]. Chemically, biofuels contain long chains of mono-alkyl esters [1]. They are produced and obtainable in solid, liquid or gaseous state from forestry, agriculture, municipal waste and fatty acids [4]. Maize, oats, potatoes, sugar beans, sugar roots, rapeseed oil, palm oil, soya beans, barley, alga, wood, forest residue, grass and more, may all be used to produce biofuels [5]. Biofuels are safe, renewable, ecological and conservational. From 2004, the production of biodiesel has grown to 100 million liters per year in the United States of America (USA) [2]. The growth was greater in Europe at 2 billion liters in a year. Countries such as South Africa, Japan, India and Australia are still investigating the prospects of biofuels, and have small productions compared to the USA and Europe [2]. On the world scale, the production of biodiesel increased to 3.9 billion liters by the end of 2005 [6]. Comparatively, biodiesel and petroleum diesel differ in the energy levels, reaching up to 14% less energy in vegetable oils, thus producing lower engine speeds and power output. Biodiesels have also been shown to have lower pH levels than petroleum diesel. This threatens the structural integrity of the engine that could result in corrosion of critical engine components [7]. Additionally, the use of biofuels produces...
sulphur and nitrogen oxide emissions, but in comparison to petroleum diesel, biodiesels have reduced emission of hydrocarbons, carbon monoxide (CO), smoke and particulate matters [8]. This complies with stringent environmental standards such as Euro 6 being imposed on new internal combustion engines. Studies have been conducted, particularly on engines to determine emission properties, fuel consumption, and performance with the use of biodiesel. Biodiesel’s high viscosity has been reported as one of its major disadvantages [9]. High viscosity affects fuel injector operation. This problem is worsened at low temperatures. Biodiesel is also less combustible than petroleum diesel. In some instances however, depending on the raw material used, biodiesel has a slightly larger cetane number, a property that determines fuel quality and ignition delay. However, flash point is generally greater in biodiesel than petroleum diesel [9]. The common failure of biodiesel in terms of complete combustion results in nitrogen and sulphur oxide emissions that reduce overall power output. On emissions, a Cummins ISBe6 direct injection engine was tested using palm oil, soybean, cotton seed, rape seed and waste cooking oil [10]. Particulate matter emission reductions were up to 69% when compared to petroleum diesel, dry soot emission reductions of up to 83%, carbon monoxide emission reductions in the range 4% to 16%, while hydrocarbons were reduced by 67%. Studies also revealed that nitrogen oxides emissions increased by up to 23% in comparison to petroleum diesel [10]. Investigations are in progress to try and reduce these emissions. Herreros et al. [11] tested methyl and ethyl esters with 30% and 70% content of biodiesel on a common rail injection diesel engine. Results revealed that the type of alcohol used in the biodiesel production has no effect on nitric oxide emissions and the opacity of the smoke. Thus the base cause of the emissions with the use of biodiesel originates from the core properties of the fuel. Tests on a Petter engine for fuel consumption and emissions with the use of sunflower oil and olive oil based biodiesel was conducted in 2001 [12]. The research produced opposing results to discoveries made on the Cummins ISBe6 engine [10]. Fuel mixtures used contained 10%, 20% and 50% vegetable oils. The results from the stationary engine revealed a decrease in nitric oxide emissions with biodiesels as opposed to previous studies. It was deduced that this result was due to the higher cetane number of biodiesel. Poly aromatic hydrocarbons were proven to be responsible for high emissions of nitric oxides [12]. Results indicated that reduction in aromatics led to reduced temperatures and therefore lower nitric oxide emissions. However, volumetric fuel consumption was found to be higher in biodiesel than petroleum diesel [12]. Investigations on a six cylinder direct injection engine [13] revealed that the increase in the percentage of biodiesel in blends decreases the torque and the overall power output. Pure biodiesel and blends of 80%, 70%, 50%, 30% and 20% were used. 5% decrease in torque was obtained using pure biodiesel together with a power decline of 3%. High density accounted for the higher specific fuel consumption, averaging at 16% [13]. Use of biodiesel is restricted at low temperatures, more so for biodiesel produced from animal fats [14]. The lower volatility may increase difficulties of cold engine starting. Fuel filters may be susceptible to blockage from loose particles in such blends.

Therefore, investigations of different biodiesel blends, particularly their properties and effects on engine performance, are important to fully understand the viability of biodiesels as replacement fuels. This investigation seeks to contribute data that indicate whether biodiesels or blends of ULSD and biodiesels made from sunflower oil are viable options in fuelling diesel engines. Obtained results will form the basis of developing a blend that will be used to test performance on a 2.3L Toyota diesel engine. The basis for comparison remains performance using pure ULSD.

II. DESCRIPTION OF EXPERIMENTS

A. Biodiesel Production

Biodiesel was produced using a batch process. A 6:1 molar ratio of 98% pure methanol to pure sunflower oil was used in addition to 1% w/w sodium hydroxide pellets. The reactants were mixed in a round bottomed flask at 60°C for 2 hours. Resulting biodiesel was cleaned with warm brine made from 40g of salt per liter of water, at a ratio of 1:2 of saltwater to biodiesel since the soap forming impurities in the biodiesel attached to the salt water and settled at the bottom of the mixture. This was repeated until the water was clear. The biodiesel was then dried by adding magnesium sulfate (MgSO₄) until solid lumps were formed and were filtered out.

B. Fuel Characterization

Prior to using biodiesel and its blends in the diesel engine, the fuel must be characterized to ensure that properties comply with those of ULSD. Biodiesel properties must also comply with ASTM standards. Calorific values, which indicate the energy content of the fuels, were determined using a Cal2k Eco bomb calorimeter. The flash point was established using a crude method where a fuel sample was heated on a stove with magnetic stirrer, while its temperature was continuously monitored using a thermometer. A flame was ignited at the mouth of beaker with the sample. The minimum temperature at which the fuel ignited was recorded. This procedure was repeated to obtain mean values. The acidity of the fuels was determined with the aid of a pH meter. Buffers were used for calibration. An estimate of the chain lengths was obtained by analyzing the integrated peaks on the proton or carbon spectrum of the fuel specimen for sunflower oil; biodiesel and the ULSD using Nuclear Magnetic Resonance (NMR). Mass Gas Chromatography (MGC) was used to establish the components present in the biodiesel produced.

C. Engine

The overall aim is to develop a fuel blend that can be used for performance testing in a 2003 Toyota 2.4L diesel engine under varying load conditions. This naturally aspirated compression ignition engine, with no supercharging or turbocharger, has a 22.2:1 compression ratio with a bore and stroke of 92mm. The engine has a 4 in-line longitudinal cylinder configuration. Some performance parameters and specifications for the engine are provided in Table 1. The engine has maximum power output of 74 kW and a maximum torque of 200 Nm.
III. RESULTS AND DISCUSSION

A. Biodiesel Fuel Characterizations

Measurements were made according to relevant ASTM and EN standards. This insured the structural integrity and safety of the engine.

**Calorific Values**

Fig. 1 shows the results of the bomb calorimeter tests for pure ULSD, pure biodiesel and 5% to 50% blends in increments of 5%.

![Calorific values of ULSD, sunflower oil and biodiesel blends](image)

The horizontal axis shows the specimens that were tested. The horizontal nature of the plots shows the accuracy and reliability of the measurements. It was found that the ULSD contained the highest calorific value on a weight basis. This is in agreement with previously published results [9]. The difference in calorific value between biodiesel and sunflower oil was small compared to the large deviation of the values for the blends. The difference in the calorific values between the pure sunflower oil and the biodiesel is due to the unsaturated fats or esters in the sunflower oil, which generally produce lower energy content. One of the reasons could be that the conversion from sunflower oil free fatty acids to mono-alkyl methyl esters was incomplete. Similarly, the difference in the calorific values between biodiesel and ULSD is due to unsaturated bonds in the methyl esters not present in ULSD. The higher the proportion of the non-saturation in the biodiesel, the greater is the difference in calorific value when compared to the ULSD. The increase in concentration of biodiesel in a fuel sample lowers its calorific. The value tends to that for pure biodiesel. As compared to ULSD, the lower calorific value would lead to higher fuel consumption. These results also suggest a linear relationship between the calorific value and the blending proportion as shown in (1),

\[
CV_p = CV_{ULSD} - p(CV_{ULSD} - CV_{PBD})
\]

where \(CV_p\) is the calorific value of blend with proportion \(p\) of biodiesel, \(CV_{ULSD}\) is the calorific value of ULSD and \(CV_{PBD}\) is the calorific value of pure biodiesel.

**Flash Point**

According to ASTM Biodiesel Standard D 6751 [15], the minimum flash point for biodiesel should be at 130°C. The European Biodiesel Standard EN 14214 for vehicle use and EN 14213 for heating oil use state that the minimum flash point for biodiesel must be 120°C [15]. Fig. 2 shows the flash points obtained in this investigation. These comply with the standards and occur above the limits set by ASTM and EN standards. The flash point of biodiesel (182.82°C) is almost twice that of ULSD (95°C). Again, this is attributed to double or triple bonds that may still exist in the biodiesel. The advantages of higher flash points in biodiesel include increased safety, making it easier to transport compared to ULSD, lower fire hazard, safer storage and reduced chances of uncontrolled detonation.

![Flash points of ULSD and biodiesel blends](image)

An increase in the concentration of the biodiesel resulted in an increase in flash point. Thus, inefficiencies in ignition quality using biodiesel are high. This will result in increased operation heat, higher losses, larger pressures and temperatures and reduced overall cycle efficiency.

**Acidity**

A fuel with a low pH value poses a threat to some of the engine’s operating components, primarily the fuel injection equipment. From the procedure followed using a calibrated pH meter, the pH value of biodiesel was found to be 6.12 which was lower than that of ULSD at 7.07. Pure sunflower oil is comprised of three fatty acids which increase the chances of having high acidity levels in biodiesel. Complete conversion from fatty acids to methyl esters will minimize acidity levels, but incomplete conversion will leave traces of the fatty acids and result in low pH values. The acid number of biodiesel is also dependent on the type of vegetable oil used and fatty acids it contains. The acidity may also be influenced by the production process and traces of soap formation from the methanol and the sodium hydroxide.
used.

**Sulphur Content**

The sulphur content of the biodiesel is limited to 0.05 % according to ASTM D 6751 [16]. The tests conducted on biodiesel samples and the ULSD fuel revealed low amounts of sulphur in the fuels. Approximately 0% sulphur was found in the ULSD test sample. Combustion products will therefore have low oxides of sulphur that have the potential to dissolve forming sulfuric acid. The average sulphur content measured in pure biodiesel was 0.057%. This was approximately 12% more sulphur than the stipulated limit.

**Density**

The density of the biodiesel did not vary significantly after trans esterification since the densities of methanol, at 791 kg/m³, and sunflower oil, at 918.8 kg/m³, are similar to the density after trans esterification. B100 is restricted within the range of 860 and 900 kg/m³ [16]. The calorific value, as discussed previously, is affected by the density thus affecting the engine air fuel ratio. Since fuel injection is measured by volume as opposed to mass, a fuel that contains a higher density has a higher mass in the same volume. Therefore, the density of the fuel injected will have a direct influence on the power output. Fig. 3 illustrates the densities of ULSD and biodiesel blends.

![Fig. 3: Densities of ULSD and biodiesel blends](image)

With an increase in biodiesel concentration, there is a decrease in density, approaching that which was established for pure biodiesel. This higher density value in the ULSD and biodiesel blends is an indication of the position of the protons in the chemical structure associated with each peak, and the integration values under each peak are provided. The integration provides the relative chemical group composition. Fig. 4 shows the results of a typical proton spectrum obtained for pure sunflower oil. If methylium (CH₃) is regarded as a point of reference, whose peak is represented approximately between 0.6 and 0.8, the integral must be divided by 3 to represent the 3 protons in methyl. The number of carbons was estimated using the proton spectrum by identifying the structure of the compound represented by each peak according to the chemical structure of the free fatty acids that make up sunflower oil. Since the peak between 0.6 and 0.8 ppm represents methylium (CH₃), for every 3 protons, there is 1 carbon in the chain. The peaks between 1.5 and 3 ppm are characteristic of methylene (CH₂) therefore, for every 2 protons, there would be 1 carbon in the structure. For the rest of the peaks, carbon content on 1:1 was assumed as carbon hydrogen (CH).

![Fig. 4: NMR proton spectrum for pure sunflower oil](image)

The NMR results give a reasonable estimation, since each fatty acid present in the sunflower oil contains approximately 18 carbon atoms, thus in a triglyceride, the values obtained for the number of protons and carbons would be multiplied by 3.

Fig. 5 illustrates the results of the carbon spectrum from the NMR analysis of the pure biodiesel produced. It must be highlighted that the glyceryl, initially present in the pure sunflower oil between 4 and 4.5 ppm is no longer present in all the samples of biodiesel. This is an indication of triglyceride break down into smaller chains. From the spectrum, an estimation of the average number of carbon and hydrogen atoms in the test specimen may be established. This is done by standardizing the NMR integration to the methyl ester resonance. This resonance is known to be equal to 3 hydrogen atoms. For the first sample, the crude integrals measured 7.93 thus it can be estimated that an integration of approximately 2.64 corresponds to 1 hydrogen atom. Using these estimates, the average formula for the biodiesel sample was found to be CₓHₓOₓ. The ratio of the polyunsaturated fats to the monounsaturated fats was estimated using the integrals of the peaks at the doubly allylic integrals between 2.6 and 2.8 ppm as well as the alkene peaks between 5.1 and 6.6 ppm. The peak of the allylic must be multiplied by 2 since there is approximately
twice the number of alkene hydrogen atoms as allylic. The ratio of poly/monounsaturated fats may be calculated by dividing the value of polyunsaturated integral by the monounsaturated integral. 2.85/1.75 = 1.63. Therefore, the estimated ratio of the polyunsaturated to monounsaturated fats for this sample is 1.63:1. The chemical formula for another biodiesel sample produced C_{19}H_{36}O_{2} and an estimated ratio of polyunsaturated to monounsaturated fats was 1.04:1. A third biodiesel sample produced C_{19}H_{36}O_{2} and an estimated ratio of polyunsaturated to monounsaturated fats of 0.86:1.

Gas Chromatography (GC)

GC is an accurate tool for analyzing biodiesel before, during and after production. The use of mass spectrum detectors eliminates ambiguities about various materials since the mass spectrum unique to individual components may be established. In biodiesel analysis, it is used to monitor the free glycerin and unrelated mono-glycerides, diglycerides and triglycerides. The gas spectrum for pure sunflower oil was not obtainable due to the temperatures at which the gas chromatograph was set. The initial temperature was set at 50°C and the final temperature at 300°C. The sunflower oil was found not to evaporate in the specified temperatures due to the high number of unsaturated bonds in the structure. This results in high boiling temperatures. Thus, comparison to pure sunflower oil is omitted. Fig. 6 illustrates the gas chromatography spectrum of ULSD indicated in blue, and the spectrum for the biodiesel is indicated in black. The chromatography was run for approximately 30 minutes, up to a point where peaks were no longer present. From the graph, it is clear that the ULSD contains too many components, generally irresolvable by mass spectrum.

Biodiesel is indicated to be made up of one major component or a collection of compounds with similar characteristics since the peaks represent a cluster or group of similar compounds. The component break-down for biodiesel would be most effective at 24.186 minutes, as this is the point where most of the biodiesel, approximately 82.5% composition, is located as indicated in Table II. The remainder of the peaks is negligible, as they could be an indication of contamination in the fuel.

At 22.162 minutes and 24.304 minutes, 7.24% and 4.21% of the fuel’s composition are present respectively, and may also be taken into account as important. Blending the biodiesel in the ULSD, at various concentrations would simply result in a spectrum that contains both curves with their characteristics fused. Between 2 and 20 minutes, the blended fuel would remain irresolvable. Fig. 7 shows the mass spectrum for another biodiesel sample. The same peaks were obtained as with the initial GC, however, there was a shift on the minor axis, thus the peaks do not occur at the same time. No glycerides were located in the spectrum, thus indicating a break in the triglyceride structure. The most significant peaks on the biodiesel spectrum occur just before 20.5 minutes and at approximately 22 minutes. The components at these peaks are provided. An analysis of the peak at 20.4 minutes was established to be 7.24% palmitic acid methyl esters. This was at an accuracy of 91%. This ester possessed no double bonds, and is in correlation with the initial assumptions of palmitic acid in the biodiesel. At 22.158 minutes it was found that oleic acid methyl esters were present and at 22.342 minutes, it was found that the peaks represent stearic acid methyl esters. This indicates that the initial sunflower oil was high in oleic acid when compared to palmitic and stearic acids.
However, it must be mentioned that these were estimates, and components with similar structures may be mistaken. The peak at 22.5 minutes was found to be an octadecanoic acid methyl ester. This was at an accuracy of 70%. Other components were found in the biodiesel sample which included methyl group and chlorine. The methyl is due to the reactant methanol and traces that remained, and the chlorine may be a result of the washing process, where warm salt water was used. The solvent, which evaporated at the initial stages of the analysis, as it was chosen due to its low evaporating temperatures, also contained chlorine, and may have influenced this. However, the solvent was only used in the diluted samples. The reduced density in the biodiesel from its initial state as sunflower oil is justifiable, since the triglyceride is indicated to have broken down to methyl esters of chains of approximately 19 carbons in length. The broken down structure also contributes to the pH number in biodiesel, though slightly acidic, not largely variant from that of ULSD. This break down in structure will improve biodiesel properties in terms of higher calorific values than pure sunflower oil, as was established using the bomb calorimeter. The energy content may have been influenced by some unsaturated bond still contained in the biodiesel, justified by the structure of the oleic acid methyl ester, seemingly having unsaturated bonds.

IV. CONCLUSIONS

It can therefore be concluded that:

- The batch process used produced biodiesel with an average chain length of 19 carbons.
- Physical properties of the biodiesel blends were found to lie between those of pure sunflower oil and ULSD.
- Lower density and calorific value of biodiesel and its blends will result on higher fuel consumption when compared to ULSD.
- The high flash point of biodiesel compared to ULSD demands high working pressures and temperature combined with timing adjustment for optimum performance.
- High sulphur content and lower pH than ULSD is a threat to engine structural integrity especially for fuel injection systems when using biodiesel.

REFERENCES