Cetane Number and Thermal Properties of Croton Oil, Biodiesel, 1-Butanol, and Diesel Blends

F. Lujaji, A. Bereczky, Cs. Novak, and M. Mbarawa

Abstract— **Vegetable oil derived fuels for diesel engines are becoming important as alternative to petroleum diesel fuels due to their environmental friendliness and availability. Ignition quality in compression ignition (CI) engines is influenced by thermal characteristics and fuel properties. In this study, the effects of vegetable oil transesterification and vegetable oil-1-butanol-diesel blend on fuel properties, cetane number (CN), and thermal characteristics were experimentally investigated. Methyl ester (biodiesel) and 10% vegetable oil-10% 1-butanol-80% diesel blend was prepared from croton oil (CRO). CN was measured in a CFR F-5 engine, and a thermogravimetric analysis (TG), as well as the determination of fuel properties of croton oils, biodiesel, and blend were carried out. It can be observed for vegetable oils that they possess low volatility characteristics, low CN and high viscosity different from those of biodiesels, blends, and diesel fuel. It was observed that biodiesels and blends exhibit similarities with diesel in the fuel characteristics, CN, and TG curves**.

***Index Terms*— 1-butanol, biodiesel, Cetane number, fuel properties vegetable oil.**

I. Introduction

Diesel engines are used in agriculture, transportation, and industries. The known petroleum reserves are predicted to become depleted in the near future. Emissions from petroleum diesel exert negative effects on the environment. The drive towards clean energy economy is therefore both indispensable and inevitable. Vegetable oils in this regard provide an opportunity to replace a proportion of the petroleum diesel usage in compression ignition (CI) engines in order to achieve significant emission reduction. In addition to emission reduction, vegetable oils are available locally, with the potential of creating jobs and providing energy security.

The use of vegetable oils in a diesel engine is as old as the diesel engine itself. German scientist Rudolf Diesel, inventor of the CI engine, tested vegetable oil in one of his engines about 100 years ago [1-4]. Vegetable oils consist mostly of triglycerides. Triglycerides are inherently viscous. High viscosity and poor volatility present major challenges to running modern diesel engines on vegetable oils. It is reported from the literature [2], [5-9] that CI engines that run on vegetable oils achieve lower peak power and torque, as well as lower engine speeds, and that these fuels cause injector coking, filter clogging, ring sticking, and thickening of lubrication oil.

Different methods can be used to improve the fuel properties of vegetable oils. These are transesterification, pyrolysis and catalytic cracking, microemulsions, and dilution with diesel fuel [6], [10-12]. Among these methods, transesterification is a method commonly used to lower the viscosity of vegetable oils [2-4], [10], [13].

Biodiesel manufactured by means of the transesterification method exhibits improved fuel properties as compared to its corresponding oil. Biodiesel shows improved volatility characteristics approaching those of petroleum diesel fuel [14]. Improved volatility and fuel properties lead to an improved cetane number (CN) [2].

It is reported from the study by Chotwichien et al. [15] that biodiesel-butanol-diesel (10% palm oil ethyl ester-5 % butanol-85 % diesel) blends record better fuel properties, such as fuel stability. From the literature, experimental works on three components (biodiesel-alcohol-diesel) as fuel for diesel engine have been carried out [16-18].

CN is the parameter used to determine the quality of diesel fuel; it is proportionate to the fuel ignition delay time in CI engines. A fuel's CN rating can be applied to determine ignition characteristics of biodiesel fuels [19]. Thermal analysis can be used to provide information on the thermodynamic characteristics of fuels, that is, temperature dependent properties and thermal decomposition [20]. Thermal analysis includes thermogravimetric (TG) analysis and derivative thermogravimetry (DTG). These techniques are used to determine fuel thermal decomposition and combustion characteristics [21].

In this work, CN and thermal properties were experimentally determined. The main objective was to study the effects of transesterification and higher alcohol-diesel blends of oils on CN, thermal characteristics, and fuel properties of vegetable oils. Vegetable oil investigated in this study was *croton megalocarpus* oil (CRO). Croton methyl ester (CRME), and 10% Croton oil-10% butanol-80% diesel blend (10% CRO-10% BU-80% D2) was studied.

II. Experimental Procedure

A. Materials

Croton megalocarpus oil was supplied by Diligent

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Tanzania Limited. The chemicals used were analytical reagent grade: 1-butanol, sulphuric acid, potassium hydroxide, deionised water, and methanol. Certified reference fuels were used and diesel obtained from a local petrol station (Budapest, Hungary) was used.

B. Procedure

Transesterification

A base catalyzed transesterification reaction was used for methyl ester conversion of CRO. Transesterification reaction parameters derived from the literature were used for the methyl ester conversion of CRO [22].

Blend preparation

Oil-butanol-diesel blend was prepared by mixing the components at room temperature. On a volumetric basis, 10%, 10%, and 80% of croton oil, 1-butanol, and diesel respectively were poured into 1000 ml beakers and stirred until they mixed. The uniform mixture of croton oils-butanol-diesel (10% CRO-10% BU-80% D2) was subsequently taken for further analysis.

Cetane number measurements

A Waukesha CFR F-5 engine was used for CN number investigation. The engine was operated under the following conditions: engine speed 900 rev/min; coolant temperature 100 ˚C; intake air temperature 65.5 ˚C; injection timing of 13 degrees before top dead centre (BTDC); fuel injection pressure 10.3 MPa. The ignition delay was set to 13 degrees by adjusting the compression ratio, so that combustion started at top dead centre (TDC) as specified by the American Society for Testing Materials (ASTM) 613. Table 1 shows the engine characteristics.

The engine was allowed to run on diesel for 1 hour to ensure consistent operating conditions. All samples and the reference fuel were filtered. The test sample was then introduced into one of the three fuel tanks raised above the engine; a fuel selector valve was used to select fuel from one of the three tanks and to select the fuel to flow from the burette in order to determine the fuel flow measurements. The fuel burette was rinsed with the test fuel and the air in the fuel line was purged. The fuel flow rate was adjusted to 13 ml/min, by the use of a flow-rate micrometer and a stop watch; subsequently the readings were noted. The ignition delay was set by adjusting the compression ratio by the use of a hand wheel. The injection advance was set to the required level. The engine using the test fuel was allowed to run for more than 5 minutes in order to establish stable injection advance and ignition delay readings. The handwheel readings were then recorded.

The lower reference fuel was then introduced into an empty fuel tank (handwheel readings were used to determine the closest CN of the reference fuel to that of the sample by comparing the handwheel readings from previous experiments). The fuel lines were flushed and the same procedure that was used on the sample was then followed for the lower reference fuel. The next upper reference fuel (that would cause the sample handwheel reading to bracket with the first reference fuel handwheel readings) was then selected (taking into account the CN difference between the two reference fuels, which was not to exceed 5.5). It was then introduced into the third tank; flushing was carried out. Adjustments on the fuel flow, injection advance, and ignition delay were then performed as in the sample and the first reference fuel.

The CNs of the samples was then calculated by an interpolation of the compression ratio handwheel readings and the CN of the reference fuels.

Thermal properties

A TG test was carried out by using TA instruments (TG 2050 CE); measured amounts of samples were placed on a platinum pan attached to the instrument. The instrument was connected to a personal computer where the sample environment and measurement method were controlled. The thermogravimetric (TG) and the time derivative of % mass loss (DTG) curves were obtained. The tests were carried out in a nitrogen gas environment at a flow rate of 10 cm^3/min, and a temperature range of 30 ˚C to 700 ˚C.

Table 1: Engine parameters

Item	Description
Crankcase	Model CFR-48D, Cast Iron
Cylinder head	Cast iron, pre-combustion chamber with turbulent passage, variable compression plug passage, integral coolant
Compression ratio	8:1 to 36:1 Variable by external hand wheel assembly
Cylinder bore	82.55 mm
Stroke	114.3 mm
Displacement	611.73 cm^3

III. Results and Discussions

Fuel properties

Some of the fuel properties of vegetable oils, biodiesels, and blends, such as their viscosity, density, and calorific value, were measured by standard methods; the results are tabulated in Table 2. It can be observed that vegetable oils possess a low gross calorific value, high viscosity, and slightly higher density than methyl esters and vegetable oil-butanol-diesel blends. Methyl esters and blends yield comparable values of viscosity and density values to diesel fuel, but methyl esters possess a lower gross calorific value than diesel and the blends.

The heat of combustion refers to the measure of energy content in the fuel. The experimental results are depicted in Table 2. The blend 10% CRO-10% BU-80% D2 was observed to record the highest gross calorific value of 44.09 MJ/kg apart from 45.54 MJ/kg of D2 fuel. The energy content of oils depends on the place where they are grown, the season, composition, and other factors. The calorific values of vegetable oils were observed to be lower than those of biodiesels. For methyl esters, the heat content increases as the length of the fatty acids chain increases. The presence of a significant amount of oxygen contributes to the low energy content of biodiesel fuels.

Viscosity is the measure of internal fluid friction which tends to oppose any dynamic change in the fluid motion at a given temperature. The viscosity values observed are depicted in Table 2. Croton oil was observed to display high viscosity values, about 6 times more than the ASTM limits.

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The croton methyl ester and the butanol blend were observed to exhibit viscosity values within the ASTM limits.

Table 2 Fuel properties:

Test	Cetane Number	Gross Calorific Value H_0 MJ kg-1	Viscosity mm^2 s-1 at 40 ˚C	Density kg m-3
Test Methods	ASTM D 613	ASTM D 240	ASTM D 445	ASTM D 1298
Limits	47 <	-	1.9 - 6.0	-
CRO	40.7	39.65	33.38	920.00
CRME	46.6	39.95	4.78	865.00
10% CRO-10% BU-80% D2	52.8	44.09	3.82	831.76
D2	54.6	45.54	2.30	823.20
BU	17.0	36.94	2.63	811.95

The density of vegetable oils depends on their origin and composition. However, their density is generally higher than that of methyl esters and diesel fuel. Table 2 records the values of the density of the croton oil, methyl ester, butanol blend, diesel fuel, and 1-butanol alcohol; it can be observed from the results the croton methyl ester shows the minimum density value of 865.00 kg/m^3. The diesel fuel sample was observed to have a density value of 823.20 kg/m^3 which is lower than that of the croton oils, methyl ester, and butanol blend.

Croton oil-butanol-diesel blends record results close to those of diesel fuel in terms of viscosity, density, and calorific values; this may be due to the high quantity of diesel (80%) in the blends. The properties obtained from the experiments using vegetable oils and methyl esters are in agreement with the values cited in the literature reviewed [23- 24].

Cetane number

Fig I, illustrates the measured values of the CN of the vegetable oils, biodiesels, and blends. It was observed that the vegetable oils have a low CN; this is due to the presence of bulkier molecules in the triglycerides which have a high viscosity. The low volatility and high viscosity of vegetable oil results in a longer ignition delay in the combustion chamber [10], [25]. CRO records the CN of 40.7. Comparable CN values for vegetable oils can also be observed in the literature [24].

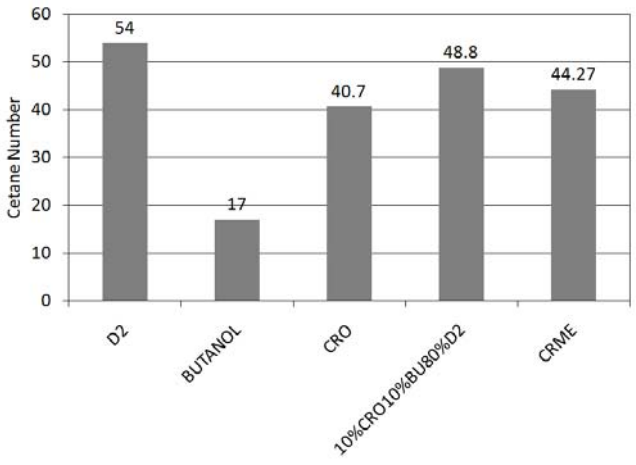

Fig I: Cetane number of diesel, 1-butanol, croton oil, butanol blend, and biodiesel

Methyl esters have a lower viscosity than their corresponding vegetable oils and it has an effect on its cetane number (CN). The CN of the tested methyl esters agrees with the literature, as transesterification reduces the molecular mass of vegetable oils, which improves volatility and lowers the viscosity of vegetable oils [2], [19]. Viscosity influences ignition delay [25-26]; hence an improved volatility and viscosity explains the improved CN of biodiesels as compared to that of vegetable oils.

It can also be observed in Fig I that croton oils-butanol-diesel blends have CN values close to those of the diesel fuel sample; this is due to the presence of 80% diesel in the blends. Petroleum diesel evidences better volatility characteristics than the vegetable oils. 1-Butanol alcohol has a low CN; this does not exert much influence because it constitutes only 10% of the total blend.

Thermal analysis

TG and DTG have been used to provide information on the thermal behavior of croton oils, methyl ester and croton oil-butanol-diesel blend. Thermal stability and volatility characteristics influence the ignition quality of fuels [21].

It was observed that diesel fuel (D2) shows about a 5 % mass loss during its first evaporation stage below 59 °C (Fig II, III, and IV), and a rapid mass loss between 59 °C and 150 °C but slows down at 210 °C (Fig II, III, and IV) with a mass loss of the remaining 95 % of the sample mass.

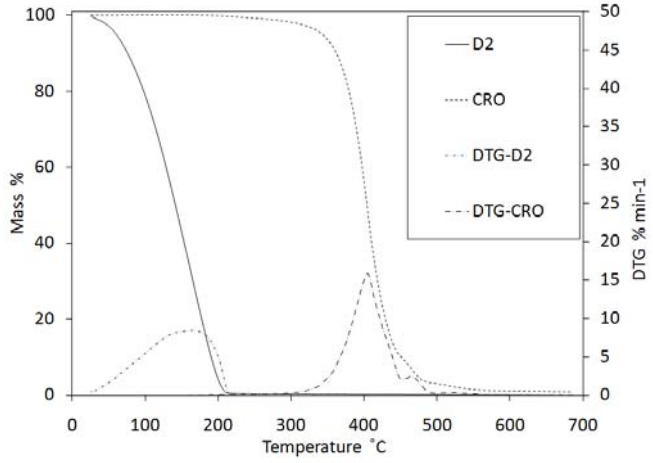

Fig II: TG and DTG curves of (D2, CRO)

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Croton oils are less volatile than diesel fuel; it record negligible mass loss below 131 °C. In Fig II, three phases of mass loss can be observed: the first phase for CRO begins from 190 °C and extends to 265 °C which corresponds with the evaporation of more volatile materials in the vegetable oils; the second phase starts from 265 °C, ending at 447 °C which corresponds to the primary decomposition; while the third phase starts from 447 °C and continues to 500 °C, which corresponds to the secondary decomposition of pyrolysis products derived from the second phase.

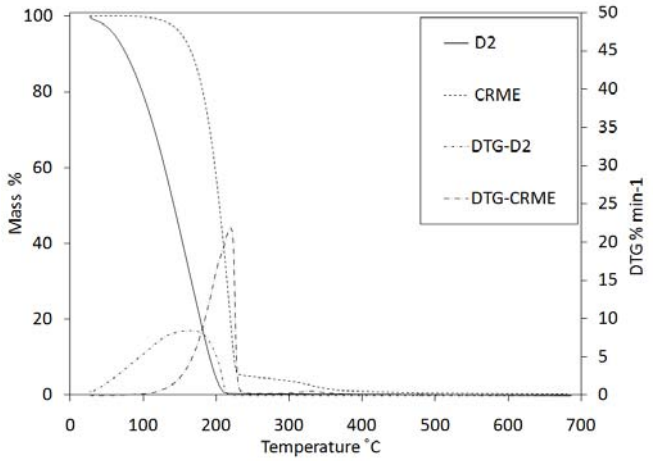

Fig III: TG and DTG curves of (D2, CRME)

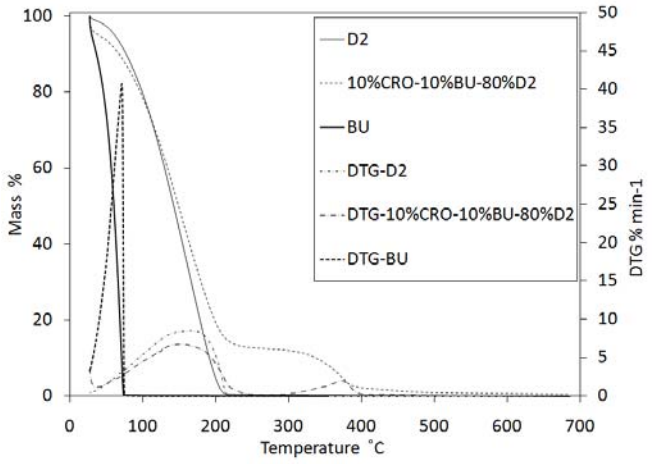

Fig IV: TG and DTG curves of (D2, BU, 10% CRO–10% BU–80%)

The volatility behavior of croton methyl esters is comparable with that of diesel fuel. Fig III depicts a negligible evaporation of CRME below 110 °C. It can be observed in Fig III that the methyl esters are characterized by one major mass loss stage depicted by high amplitude peaks, followed by a negligibly small flattened peak. This explains that the transesterification process improves and smoothens the volatility characteristics of vegetable oils: that is, only one major mass loss activity can be observed in the methyl esters TG curves as compared to the TG curves for vegetable oils.

Croton oil-butanol-diesel blends record thermal behavior which is comparable with diesel. The mass loss behavior of the blends can be categorized into three main steps. The first step corresponds with the mass loss of about 10% (Fig IV) at a temperature below 59 °C. The second step is also similar for all the blends; it extends from 59 °C to 226 °C and corresponds with the mass loss of about 78%. The third step occurs in the temperature range of 226 to 700 °C, where further mass loss is observed in Fig IV; this part corresponds with about 12% of the sample's mass. It is clearly noticeable in Fig IV that the behavior in these steps is influenced by the type and quantity of components in the blend. It can be suggested that the first step is dominated by butanol evaporation, the second by diesel fuel, and the third by croton oil; hence it can be further argued that there is no intermolecular chemical reaction between the components in the blends.

Vegetable oils are thermally more stable than methyl esters and blends. This is due to the much greater tension that exists in the bulky triglycerides molecules than in the methyl esters. The molecular tension and structure influence volatility and the CN. It was observed that diesel (D2) fuel is thermally less stable than vegetable oils and biodiesel; this fact was also observed by Rodríguez et al., [21]. Lang et al., [27] pointed out that high viscosity can contribute to a slow evaporation process. For blends, it can be observed that they possess similar volatility characteristics and CN values as compared to those of diesel fuel; this is influenced by a larger percentage of diesel fuel (80%) in the blends.

IV. Conclusions

The following conclusions can be deduced from the results and discussion above:

1. Volatility characteristics and fuel properties of croton oil is improved by the transesterification and the blending of vegetable oil, butanol, and diesel fuel.
2. 10% croton oil-10% 1-butanol-80% diesel blend possess a CN, thermal characteristics, density, and viscosity which are much more comparable to those of diesel fuel, than methyl esters.
3. Poor fuel properties, and low volatility characteristics, of vegetable oils are improved by the transesterification process. The fuel properties and thermal behavior of methyl esters approach those of diesel fuel.
4. The thermogravimetric analysis results agree with the CN experimental results, suggesting a strong relationship between the thermal characteristics and CN of fuel samples.

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