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Oxidation Stability and Low Temperature Properties of Rubber Seed Oil Biodiesel from Fatty Acid Composition

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Abstract: This study is aimed at determining the oxidation stability and cold flow behavior of rubber seed biodiesel from fatty acids composition. The oxidation stability was measured in terms of induction period while the cold flow properties of the biodiesel was evaluated by determining the cloud point (CP), pour point (PP), cold filter plugging point (CFPP) and low temperature flow test (LTFT). The result of oxidation stability revealed that rubber seed biodiesel exhibited an induction period of 3.13 hours. The cold flow properties of the biodiesel such as CFPP, CP, LTFT, and PP were determined to be -11.69, -7.19, -2.19 and -12.15 respectively. This study depicts that rubber seed biodiesel has good oxidation stability when compared to a minimum of 3 and 6 hours stipulated by ASTM standardand EN respectively for biodiesel. The cold flow properties shows that the biodiesel exhibit appreciably low temperature properties and so can be effectively used in cold weather without clogging the engine filter.

1. INTRODUCTION

Biodiesel is increasingly becoming an alternative fuel for diesel engines (Ezeanyanaso*et al*, 2012). Biodiesel consists of a mixture of alkyl esters of long chain acids. It is derived from the reaction of vegetable oils or animal fats in the presence of a catalyst (Kivevele and Huan 2015). Biodiesel can also be used in some conventional compression ignition engines without modification. It can also be used as heating oil (Marinkovic*et al*., 2015). The major problems of biodiesel are its high cost of production, poor oxidation and cold flow behavior stability (Yaakob*et al.,* 2014).

Cold flow behavior are characterized by the temperature at which biodiesel starts to change from fluid to solid state, resulting in performance issues. The temperature of biodiesel crystallization is higher than that of mineral diesel fuel; thus, crystal formation at moderately high negative temperatures may clog fuel filters and fuel flow line thereby resulting in fuel starvation and operability problems during cold weather (Liu *et al*., 2015). Cold flow behavior is dependent on fatty acid composition (Zuleta*et al*., 2012). The cold flow behavior of biodiesel is generally assessed through its pour point (PP), cloud point (CP), and cold filter plugging point (CFPP).

The oxidative stability of biodiesel is a very important property, particularly in warm climatic region. This property is a direct measure of the shelf life of biodiesel during storage under atmospheric conditions. Biodiesel oxidation can be attributed to a number of factors such as the number of double bonds present and the existence of allylic (alkene hydrocarbons) and bis-allylichydrogens. The low oxidation stability of biodiesel is principally due to the presence of unsaturated alkyl esters which can easily oxidize to acids, aldehydes, ketones, esters, peroxides and alcohols leading to the formation of insoluble gums and sediments (Musa *et al.,* 2016). Biodiesel is oxidized by the presence of unsaturated fatty acids, and subsequently the double bonds abnormally react with oxygen (Kivevele and huan, 2015). The increase in the concentration of linoleic and linolenic acid will lead to the reduction in oxidation stability of biodiesel. However, lowering the oxidation stability negatively affects acid value and kinematic viscosity. On the contrary, biodiesel with high amount of unsaturated fatty acids has better cold flow properties (Yaakob*et al*, 2014). Therefore, biodiesel can be degraded. When biodiesel is oxidized, the subsequent dregs can affect the performance of the fuel flow system, as well as plug the fuel filter and cause injector fouling, which result in engine start-up problem (Zuleta*et al.*, 2012). Oxidation causes biodiesel to be acidic, causing fuel framework erosion. Oxidation negatively influences fuel properties such as viscosity and cetane number. Other properties also depend on the content of saturated and unsaturated fatty acid methyl esters (FAME) in the oil (Liu *et al.*, 2012). Biodiesel fuels have saturated and unsaturated (for examples, polyunsaturated and monounsaturated) fatty acid ester (Hassan and AbulKalam 2013). But oxidation stability and cold flow behaviour are generally relatively opposite, that is, a biodiesel that has good cold flow properties will exhibits poor oxidation stability and vice versa. The content of fatty acid compositions and properties of different biodiesel feedstock vary (Moser, 2013). The oxidation stability and cold flow properties of biodiesel from different vegetable oil such as luffacylindrica oil and soybean oil have been reportedly documented by Ozulu*et al.*, (2016) and Dunn *et al.*, (2011) respectively. The aim of this present work is to study the oxidation stability and low temperature properties of a typical Nigeria rubber seed oil biodiesel based on its fatty acid compositions.

2. METHODOLOGY

2.1 MATERIALS

The materials and equipment used includes rubber seed biodiesel, sample bottles, weighing balance, beakers, separating funnel, hand gloves, distilled water, conical flask, gas chromatograph, and mass spectrometer.

2.2. METHODS

2.2.1Determination of fatty acid composition

Rubber seed biodiesel sample was subjected to GC–MS analysis using a Gas Chromatograph (Model: QP2010 Plus, Shimadzu, Japan) attached with quadruple Mass Spectrometer (Model: HP 5973) with a capillary column of length = 30m, inner diameter = 0.25mm and film thickness = 0.25µm).About 0.1 ml was injected into the GC. The injector column temperature was maintained at 200 ^{o}C and the oven temperature was programmed linearly. Injection mode was split type at 200 ^{o}C; total and column flow were 41.2 mL/min and 1.82 mL/min respectively at a linear velocity of 49.2 cm/sec., purge flow of 3.0 mL/min, ion source temperature 200^{o}C and split ratio of 20.The identification of the peaks was achieved by retention times through comparision with authentic standards analyzed under the same conditions. Computer matching was done with the mass spectral libraries (NIST05s.LIB) provided with the computer controlling the GC–MS System.

2.2.2 Determination of Cold flow properties

Determination of Cloud Point (CP)

Verma*et al.,* (2016) predicted the CP of biodiesel based on its fatty acid composition by the using the equation given below;

$$CP = 1.44 * (\%\text{Saturated fatty acids}) - 24.8 \qquad (1)$$

Determination of Cold Filter Plugging Point (CFPP)

CFPP was calculated from cloud point values using equation (2)

$$CFPP = 1.0\,(CP) - 4.5 \qquad (2)$$

Determination of Low Temperature Flow Test (LTFT)

LTFT was computed from cloud point values using equation (3)

$$LTFT = 1.0\,(CP) + 5 \qquad (3)$$

Determination of Pour Point

Pour point can be computed from cloud point values using equation (4)

$$PP = 0.98(CP) - 5.1 \qquad (4)$$

2.2.3 Determination of oxidation Stability

Oxidation stability of biodiesel can be measured by induction period. Induction period can be evaluated in terms of concentrations of mono, polyunsaturated and saturated fractions given in the following equations below;

$$IP = 0.27\,[SAT] + 0.13\,[MONOUNSAT] - 0.09\,[POLYUNSAT] \qquad (5)$$

Where [SAT], [MONOUNSAT], and [POLYUNSAT] are the mass compositions of the saturated, monounsaturated and polyunsaturated fatty acids (%wt) respectively. Equation (5) will be valid in the tested intervals of: $7.2 \leq [SAT] \leq 92.9$; $5.9 \leq [MONOUNSAT] \leq 83.1$, and $1.2 \leq [POLYUNSAT] \leq 61.3$ respectively (Serrano *et al.,* 2014).

3. RESULTS AND DISCUSSION

3.1 Fatty acid composition

The relative compositions of fatty acid as determined by GC-MS of rubber seed oil are shown in Table 2.

Table 1: Properties of Rubber Seed oil Biodiesel

Properties	Value
Specific gravity (@15	0.882
Viscosity (mm^2/s @ 40 ^{o}C)	4.0
Cetane number	54
Calorific value (MJ/Kg)	42

The properties shown in Table 1 clearly indicate that the biodiesel properties are in agreement with ASTM standards.

Table 2: Fatty Acid Profile of Biodiesel

Fatty acid	Percent (%)
Myristic acid (C14:0)	2.87
Stearic acid (C18:0)	0.91
Palmitic acid (C16:0)	2.44
Oleic acid (C18:1)	23.64
Palmitoleic acid (C16:1)	4.97
Linoleic acid (C18:2)	44.52
Linolenic acid (C18:3)	8.11
Arachidic acid (C20:0)	6.01
Eicosenoic acid (C20:1)	6.52
Saturated	12.23
Monounsaturated	35.13
Polyunsaturated	52.63

Fatty acid profile is used to determine the chemical and physical properties of vegetable oil and its methyl ester (Da Silva Cesar, 2014). The results of the fatty acid composition in Table 2 show that linoleic acid (44.52 %) is the predominant fatty acid followed by oleic acid (23.64 %).The high percentage of linoleic, oleic and linolenic acid will lead to the reduction in oxidation stability of the biodiesel (Jain and Sharma, 2014).

3.2 Induction period

The induction period of biodiesels reveals the level of degradation. It is an important parameter that is used to determine the oxidative stability of biodiesel (Peterson *et al.,* 2000).The induction period of this study was calculated to be 3.13 h. The induction period of rubber seed oil is within the ASTM standard of 3 hours minimum IP and but less than the minimum EN value of 6 hour. The result obtained in this work shows a close proximity to 3 h and 3.65 h reported for moringa oil and tallow oil methyl ester work by Kivevele and Huan, (2015) and Donato*et al*. (2012) respectively. The induction period for rubber seed biodiesel obtained in this study shows that the biodiesel has good oxidation stability and therefore can be effectively stored for a long period of time (at least six month) without undergoing oxidative degradation.

Table 3: Cold flow behavior of biodiesel

Feedstocks	**CP**	**PP**	**CFPP**	**LTFT**	**References**
Waste cooking oil	14.5	13.7	-	-	Sharma *et al.* (2016)
Luffer cylindrical	-16	-12	-	-	Ozulu*et al.* (2015)
Soybean oil	0	-2	-2	0	Dunn*et al.* (2011)
Jatrophacarcus	4	3	2	-	Serin*et al.* (2007)
Rubber seed	7.19	12.15	11.69	2.19	This work

3.3 Cold flow properties

Cold flow properties of biodiesel are properties that are used to determine the performance of biodiesel in cold weather conditions. The cloud point of biodiesel is the temperature at which crystals start to appear when the fuel is cooled (Salaheldeen*et al*., 2015). Cloud point is a very important parameter that is used to calculate other cold flow properties like pour point (PP), cold filter plugging point (CFPP) and low temperature flow test (LTFT). From the results obtained in this study the cloud point of rubber seed biodiesel was -7.19 ^{o}C. This means that rubber seed oil biodiesel can be effectively used at temperature above this cloud point. Biodiesel with low cloud points shows good cold flow property of biodiesel.

Pour point (PP) is the lowest temperature at which the fuel becomes semi solid and loses its flow characteristics and no longer pump able; hence it is a measure of the fuel gelling point. The pour point is always lower than the cloud point (Dwivediand Sharma, 2013).The value of pour point obtained for rubber seed methyl ester is calculated to be -12.15 ^{o}C. The value of pour point obtained in this study is lower than the reported work shown in Table 3. The value is quantitatively is similar to -12 ^{o}C reported by Ozulu*et al*. (2015) for luffercylindrica methyl ester. The result obtained depicts that the biodiesel can be used in both temperate and tropical regions of the world.

Cold filter plugging point (CFPP) is the minimum temperature, at which a given volume of diesel fuel has capacity to pass through a regular filtration unit in a definite time when cooled under certain conditions. CFPP plays a vital role in cold temperate regions of the world. Higher cold filter plugging point are not desirable as it easily clogs up vehicle engines (Dwivedi and Sharma, 2013). The result of cold filter plugging point obtained for rubber seed methyl ester is -11.69 ^{o}C. Comparison of result with biodiesel from other common vegetable oil shown in Table 3 indicates that rubber seed methyl ester exhibited better CFPP with lower value. The difference in CFPP could be attributed to difference in fatty acid profile.

Low temperature flow test (LTFT) denotes the lowest temperature at which 180 mL of the test fuel can be safely drawn through a 17 µm screen at 20 kPa of vacuum in 60 seconds. It is a better approach because it takes into account the rigorous conditions within the engine (Odeigah*et al.,* 2012). The value of Low temperature flow test (LTFT) of rubber seed methyl ester obtained in this study is -2.19 ^{o}C. This result is lower than 0 ^{o}C reported Dunn *et al*., (2011) for soybean methyl ester. The low LTFT obtained in this work signifies that rubber seed methyl ester will exhibit satisfactory performance in cold weather.

4. CONCLUSION

The oxidation stability and cold flow properties of rubber seed biodiesel was estimated in this work from the fatty acid of the methyl ester. Rubber seed biodiesel exhibited good oxidation stability which is within the minimum of 3 stipulated by ASTM and but less than 6 hours stipulated for biodiesel EN. The result of cold flow properties shows that the biodiesel exhibitedgood low temperature properties and so can be effectively used in cold weather without clogging the engine filter.

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