

The effects of storage time on fuel properties of Jatropha biodiesel blends

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ABSTRACT

This study investigates the effects of storage time on fuel properties of biodiesel made from Jatropha oil and its blends with mineral diesel at different percentage compositions. The influence of storage stability on selected fuel properties such as kinematic viscosity, density, pour, cloud and flash points for Jatropha biodiesel and its blends at varying storage times were investigated using standard test methods. The biodiesel obtained through trans-esterification of Jatropha oil was blended with mineral diesel to obtain fractional samples of B20 (20% biodiesel blend), B40 (40% biodiesel blend), B60 (60% biodiesel blend) and B100 (100% neat biodiesel). Results show that kinematic viscosity and density increase for each blend over the 12 weeks of storage period. Flash, cloud and pour points decrease for each blend over the period of study. B20 was observed to be the optimum blend mix as its fuel properties were relatively unchanged over the storage period when compared to that of mineral diesel. It can be implied from the research that while properties like kinematic viscosity and density deteriorate with time; flash, cloud and pour points are observed to have improved with storage time.

Keywords: Biodiesel; storage stability; kinematic viscosity; density; flash point; pour point; Cloud point.

1. INTRODUCTION

At present, there has been renewed significance for bioenergy in order to bridge the growing gap between energy needs and its sustainable and affordable supply.^{1,2} This is due to the growing concern over the Earth's limited fossil fuel reserves,³ high demand for energy by an increasing world population, effects of greenhouse gas emissions,^{4,5} environmental pollution and degradation. This will largely reduce the adverse effects of fossil fuels burning, soften the pressure of over-dependence on fossil fuel, and reduce greenhouse emission.⁶ Bioenergy, a renewable-energy technology with the potential to mitigate greenhouse gas emissions in electricity, heat and biofuel supply, among others, has been depicted to be viable, in particular, in the electricity and transportation sectors. Moreover, one of the positive characters of biomass is its ability to be utilised to deliver a wide range of diverse biofuels and biomaterial products.⁷ Biofuels are promising renewable alternative energy sources;⁸ which have been attracting renewed interest from numerous government agencies, businesses, universities and research institutions, among others. Numerous biofuels, which include the woody products, bio-residues and crop residues such as cobs, husks, straws, stalks etc., agricultural lipids, microalgae and animal refuse, among others; have been resourcefully exploited in modern times. Although solar, wind and mini/ micro hydro dominate the renewable energy forecasts; biofuels look more promising due to new emerging technologies.⁸ They have been playing a vital role in the renewable energy sector despite the niche markets for solar, wind and mini/micro hydro.^{8,9}

Among the alternative renewable biofuels, biodiesel, a monoalkyl ester, is obtained through transesterification of

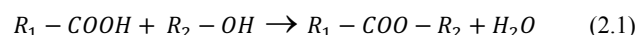
agricultural feedstock like vegetable oil, microalgae oil and spent cooking oil.¹⁰⁻¹² It is a biodegradable, non-toxic fuel with a favourable combustion-emission profile, which produces much less carbon monoxide, sulphur dioxide and unburned hydrocarbons than the mineral (or conventional) diesel.^{12,13} These facts have positioned biodiesel as a promising alternative for or an additive to mineral diesel fuel.^{12,14-17} A few research and developmental studies have been conducted on non-edible oils like spent cooking oil, waste grease, animal fats and lard.^{18,19} There are numerous numbers of other non-edible, tree-based oil-bearing seeds, which have great potential of being trans-esterified for biodiesel production.^{18,20} Jatropha (*Jatropha curcas*), one of the most promising renewable alternative sources of biodiesel,^{1,21} is a non-edible and drought-hardy small oil-bearing fruit shrub, belonging to the *Euphorbiaceae* family, which thrives in a warm climate and can grow in arid, semi-arid and wasteland.^{11,22} With little water and fertilizer, Jatropha can survive on unfertile soils with high-seed yields, which it would continue to bear for as much as 30 - 40 years.¹¹

It is expected that fuel is produced not only for immediate consumption but also for future use. The deterioration of the fuel properties of the Jatropha biodiesel blends with storage time is thus an issue that threatens its utilisation as an alternative fuel. Jatropha oil contains more or less unsaturated fatty acids, which are prone to oxidation, accelerated by exposure to air during storage, and at high temperature may result in polymerised compounds.²³ Literature is replete with storage parameters of biodiesel from different feedstocks, but none in particular on the

Jatropha curcas. Thus, this paper examines the effects of storage parameters on selected fuel properties for *Jatropha* biodiesel and its blends with mineral diesel as well as the optimum-blending ratio for good storage and thermal stabilities.

2. Materials and methods

The *Jatropha curcas* seeds used in this study were harvested in Ajagba village, Oyo state, Nigeria. The extraction was done using the soxhlet extraction method. After the oil was extracted, a trans-esterification process was carried out to convert it to its biodiesel. For the purpose of this study, an alkyl based trans-esterification process was employed. This entailed the use of sodium hydroxide as the catalyst and methanol as the solvent for obtaining the methyl ester. The first step in this process was to reduce the amount of free-fatty acids (FFA) in the *Jatropha* oil by an acid-based process. During this step, the crude *Jatropha* oil was poured into a conical flask and heated to a temperature of 60°C. A mixture of concentrated H₂SO₄ (1% w/w) with methanol (30% v/v) was heated separately at 50°C and then added to heated oil in the flask. The mixture was stirred for 1 hour using a magnetic stirrer and allowed to settle for 2 hours. This process can be expressed as:



Oil + Alcohol $\rightarrow$ Oil with reduced FFA + water

The trans-esterification process of the oil was carried out in the following sequence: 100 g of *Jatropha* oil was measured into a flask and heated to a temperature of 50°C and 1 g of sodium hydroxide pellets was measured and mixed with 20 g of methanol to prepare a solution of sodium methoxide. The sodium methoxide solution was heated to 60°C and then poured into the warm *Jatropha* oil. The mixture is allowed to settle for 24 hours in a separating funnel, and the biodiesel, which floats on top, was collected in order to separate it from the glycerol and soap by-products. Afterwards, warm water was used to wash the biodiesel to remove excess glycerol and soap, and the washed biodiesel was dried through heating to remove water from it²⁴. The process can be expressed as:²⁵



The diesel used for blending with *Jatropha* biodiesel was obtained from NNPC Mega Filling Station, Ibadan, Nigeria. Its selected fuel properties include density of 0.9028 g/cm³, kinematic viscosity of 4.6 cSt, flash point of 78°C, cloud point of 5.6°C, and pour point of -11°C. Afterwards, the preparation of *Jatropha* biodiesel blends with diesel were carried out. The designation of the *Jatropha* biodiesel-diesel blends, which indicates their percentage composition by

volume of biodiesel to mineral diesel, were splashed and blended in beakers at different quantities of B20 (20% biodiesel blend with 80% mineral diesel), B40 (40% biodiesel blend with 60% mineral diesel), B60 (60% biodiesel blend with 40% mineral diesel), B80 (80% biodiesel blend with 20% mineral diesel) and B100 (100% neat biodiesel).

2.1 Experimental procedures

Eighty tests were carried out on sixteen distinct samples over the course of 12 weeks. Samples were stored at room temperature in sealed containers. Viscosities of samples, at different storage times, were determined using a Cannon-Fenske viscometer (ASTM D445). Kinematic viscosity values were obtained from the product of the capillary U-tube viscometer's constant and efflux time. To determine the viscosity, the Cannon-Fenske viscometer was cleaned with toluene before each test in order to expel any remnants in the tube. Afterwards, the sample was introduced into the side of the tube with only one bulb. The level of sample poured into the viscometer was about the centre of the bulb and suction pressure applied by blowing into the end where the sample was introduced to raise the fluid past the upper-level mark. A stopwatch was used to record the time it took the fluid to move from the upper-level mark to the lower-level mark and the efflux time taken. The capillary U-tube viscometer's constant is 0.1 cSt/s (for the particular viscometer used). The kinematic viscosity ν can be expressed as:

$$\nu = K_v \times t \quad (2.3)$$

Where K_v the capillary U-tube viscometer's constant and t is efflux time.

The density of the *Jatropha* biodiesel and its blends were determined based on ASTM D845 standard using a pycnometer (density bottle) - a bottle of known volume, in conjunction with a digital weighing device. To determine the density, the density bottle was cleaned with toluene and dried. After drying, the density bottle was placed on a digital scale to determine its weight, which was recorded. Afterwards, the sample was introduced into the pycnometer until it slightly overflowed and the stopper applied to dispel extra fluid. The density bottle was cleaned and placed on the scale to determine the weight of pycnometer when filled with sample. The density is, thus computed using the following equation, which can be expressed as:²⁶

$$\rho = \frac{W_{p+f} - W_p}{V} \quad (2.4)$$

Where W_{p+f} is the weight of pycnometer and the blend sample, W_p is the weight of pycnometer, and V is the volume of pycnometer (50 cm³).

An electrically heated Pensky-Martens closed cup apparatus was used to determine the flash point of samples using ASTM D93 standard. With this method, an open flame was introduced to the sample as its temperature gradually increases until the sample flashes. To determine the flash point, the flash point tester was switched on and 4 ml of the test sample was introduced into the closed cup. The test range temperature was set to the maximum value of 300°C, while the gas line was opened to supply the system with propane gas. The lighter was then used to ignite the gas at the other end of the gas line. The cup containing the sample was intermittently opened and closed such that the sample temperature increases until the flash was noticed. The temperature, at which the flash occurred, referred to as flash point was noted and recorded.

The SETA™ cloud point and pour point cryostats, corked test jars and thermometer were used to determine the cloud point and pour point temperatures of samples based on ASTM D2500 and ASTM D97 standards respectively. The cryostat has 3 compartments, each with its own temperature controller. The test jars, which are 1.6 mm thick, have a line to indicate sample height of about 54 - 63 mm, fitted with a cork through which a thermometer passes to measure the sample temperature. There are three stages involved in the measurement of cloud and pour points using the cryostat. The first stage, which was the preparation of the bath, involves the opening of the well to be used for testing, removing the metal jacket container, using a funnel to fill the well with methanol, pouring a little methanol in the metal jacket such that it does not spill over when the test jar is inserted and replacing the metal jacket in the well. The second stage is the glassware assembly. At this stage, the test jar is filled with sample to be tested up to the mark on the tube and covered with a wooden cork, which has a thermometer opening at the top. Finally, a thermometer is inserted in the test jar, making sure the bulb is fully immersed in the sample, and the assembly placed in the open well. To determine the cloud point, the cryostat and automatic temperature reader were switched on. As the temperature of the bath fluid drops, with the test jar in the cooling bath, the sample is withdrawn intermittently to check for any cloudiness and when cloudiness is noticed, the temperature reading on the thermometer, referred to as cloud point was recorded. To determine the pour point, a test jar with the sample is placed in the cryostat and allowed to freeze completely. Afterwards, the corked test jar with the frozen sample was taken out of the cryostat and the cryostat was switched off. Then, the wooden cork was removed and the test jar tilted intermittently to check for the first signs of sample flow. A thermometer was used to measure the temperature at which

the sample poured and the temperature referred to as pour point was recorded.

3. RESULTS AND DISCUSSION

Kinematic viscosity, cloud, pour, and flash points, as well as the density of *Jatropha* biodiesel and its blends with diesel were determined at different storage times to examine the level of deterioration or otherwise of the biodiesel and its blends. Figure 1 shows that the kinematic viscosity values increase as storage time increases. This can be attributed most likely due to the formation of peroxides during the biodiesel reaction with atmospheric oxygen, leading to the formation of gums and sediments.²³ Moreover, it was observed that a 12.5% change in viscosity occurred for B20 during the first four weeks of storage time, which was the highest change in viscosity observed within the study duration. Also, a 0.7% change in viscosity occurred for B20 between the fourth and eighth week, which is the lowest change in viscosity observed among the blends. According to ASTM D6751, the accepted range of viscosity for biodiesel is between 1.9 - 6.0 cSt.²⁷ The B20 blend was closed to this range throughout the duration of the storage time. The viscosities for the blends B40, B60, B80 and B100 were out of this range throughout the duration of the study. Generally, the percentage changes in values of viscosity were not excessive and mostly got lower as the weeks' progress.

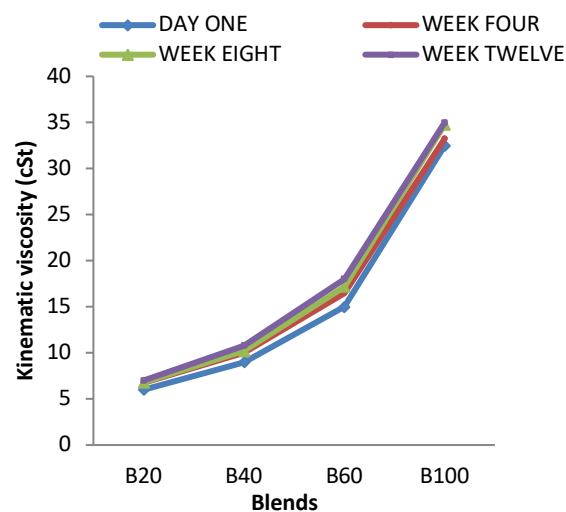


Figure 1: Variation of kinematic viscosity for different blends with storage time

Figure 2 shows that the density of each blend of *Jatropha* biodiesel and mineral diesel increases marginally with increase in storage time. The increasing rate of oxidation as storage time increases may have led to the formation of peroxides, which leads to molecular interaction of degraded biodiesels. This could be responsible for the marginal

increment in density.^{23,28} Moreover, a 1.0% change in density occurred for B20 during the first four weeks of storage time, which is the highest change in density observed within the study duration. Changes in density values were quite negligible and mostly comparable with the value of the mineral diesel (0.9028 g/cm³).

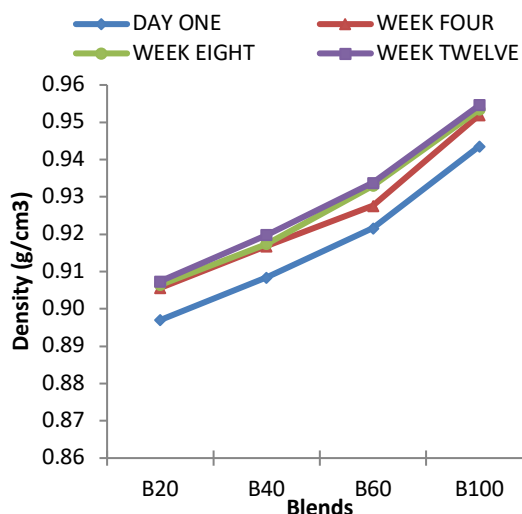


Figure 2: Variation of density for different blends with storage time

Figure 3 shows that the cloud point values increase with increase in percentage composition of Jatropha biodiesel in the blends. However, the cloud points of the blends reduce as storage time increases, which might be attributable to the oxidation of residual glycerol in the presence of peroxides²⁹. Compared to the cloud point value for the mineral diesel (5.6°C), the cloud point values for the blends were quite low on the first day of study. This got progressively better as storage time increases. The cloud point values obtained became similar to that of the diesel fuel (5.6°C) at around the eighth and twelfth weeks. Moreover, a 350% change in cloud point occurred for B20 during the first four weeks of storage time, which represented the highest change in cloud point within the study duration. Also, an 8.3% change in cloud point for B20 between the eighth and twelfth weeks was observed, which represented the lowest cloud point change within the study duration.

Figure 4 shows that the pour point values generally increase with increase in the percentage composition of Jatropha biodiesel in the blends with diesel fuel across each storage time. Also, for each blend, there was a general decrease in pour point temperature as storage time increases. Moreover, the pour point of B100 changed from 0 to -11°C between the fourth and eighth week of storage time, which is the highest change in pour point within the study duration. Also, a 12.5% change in pour point is observed for B40 between the eighth and twelfth week of storage time, which was the lowest change in pour point within the study duration. The low values of pour point compared to that of the mineral

diesel used in the blending (-11°C) may be taken as a good sign as it indicates that even at such low temperatures, the blends are able to flow.

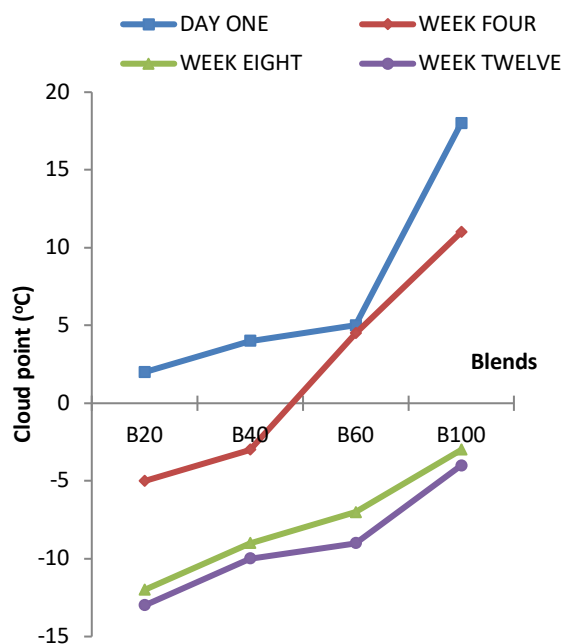


Figure 3: Variation of cloud point for different blends with storage time

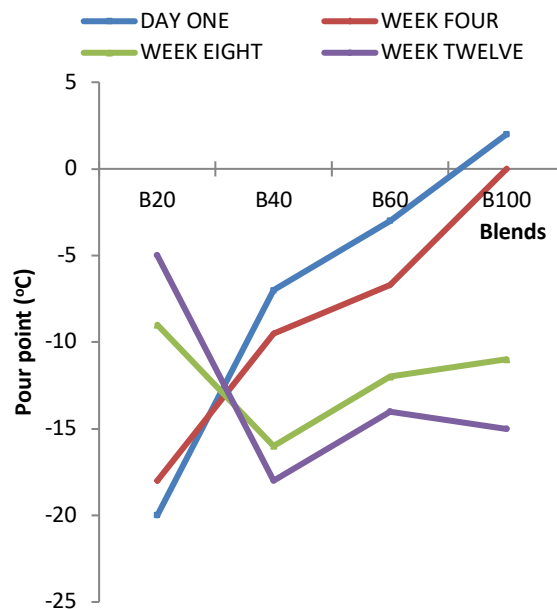


Figure 4: Variation of pour point for different blends with storage time

Figure 5 shows that the flash point values reduce as storage time increases for different *Jatropha* biodiesel blends with diesel. This may be considered interesting since the flash point of B20 at week 12 (90°C) compared favourably with the flash point of the mineral diesel (78°C) used in the study. A low, but not too low, flash point is required for complete combustion of fuel in diesel engines²³. The reducing flash point may be attributed to the presence of residual alcohol content of the biodiesel³⁰. Moreover, a 32.1% change in flash point occurred for B20 during the fourth and eighth week of storage time, which is the highest change in flash point within the study duration. Also, a 3.2% change in flash point is observed for B20 between the eighth and twelfth week, representing the lowest change in flash point within the study duration.

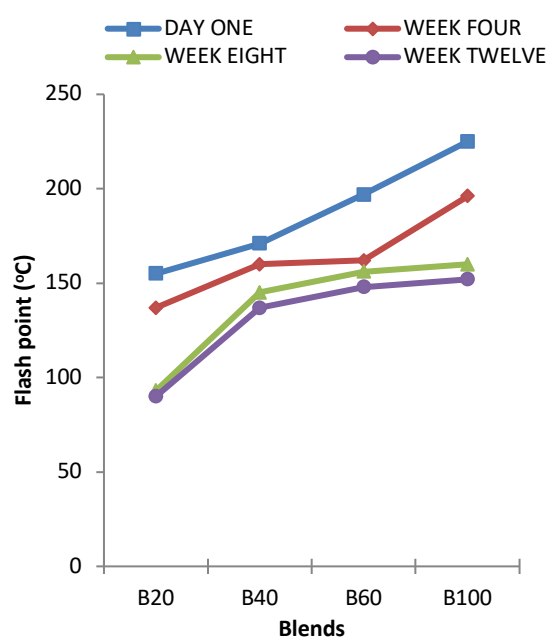


Figure 5: Variation of flash point for different blends with storage time

4. Conclusions

The effect of storage stability on selected fuel properties like kinematic viscosity, density, pour, cloud and flash points for *Jatropha* biodiesel and its blends with mineral diesel at varying storage times were investigated using standard test methods. Results show that as storage period increases, certain fuel properties deteriorated and became incomparable to those of mineral diesel. Blending *Jatropha* biodiesel with diesel fuel improves the selected fuel properties of the blends. However, the higher the percentage composition of *Jatropha* biodiesel blended with diesel, the less desirable the fuel properties of the blends obtained.

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APPENDIX

Graphical Abstract

