

Oxidation Stability of Fatty Acid Methyl Ester under Three Different Conditions

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Abstract

Maintaining fuel stability is one important criterion in sustaining the quality of fuels. This research investigated the production of biodiesel from waste groundnut oil and the oxidation stability of the biodiesel samples stored under three conditions (a vacuum, a fridge and an exposure to atmosphere) by considering their saponification values, percentage of free fatty acid, peroxide values, iodine values and viscosity. Maximum biodiesel yield was obtained at 9 methanol/oil mole ratio, 1.0w/w%Oil KOH catalyst concentration, reaction time of 60 minutes and reaction temperature of 60 °C. The results showed that biodiesel oxidation stability is adversely affected by increase in saponification value, percentage of free fatty acid, peroxide value; and decrease in iodine value and viscosity. Also, the results of these physico-chemical properties shows that vacuum is the most favourable storage condition, compared to freezing and atmospheric conditions.

Keywords: Atmosphere, Biodiesel, Refrigerator, Trans-esterification, Vacuum

1.0 Introduction

The new trend in renewable and sustainable energy production is the adoption of liquid biofuels which are obtained majorly from plants. Biodiesel is one good choice of interest in this direction because it is environmentally friendly, its production technology is simple and the raw materials needed are readily available (Ayoola, 2015; Shay, 1993; Jain and Sharma, 2010). Compare to petroleum diesel, biodiesel has lower emission profile; it has net emissions reduction in particulates, hydrocarbons, carbon monoxide and sulphur content. It has higher cetane number which improves engine performance and fuel lubricity (Ayoola, 2015; William, 2006; Galadima *et.al.*, 2008).

The triglycerides of plant/animal oils react with short-chain alcohol (methanol or ethanol), in the presence of a catalyst (mostly KOH or NaOH) to produce biodiesel and glycerol. Pure biodiesel is oxygenated (contains up to 11% oxygen), it is composed of mono-alkyl esters of long chain fatty acids produced through trans-esterification process (Ayoola *et. al.*, 2012; Demirbas., 2003; Knothe *et.al.*, 1997).

The ability of fuel to maintain its physical and chemical properties, by not interacting with its environment, during a long period of storage is referred to as fuel stability (Pinto, 2005; Su and White, 2004). Various processes, such as hydrolysis in presence of moisture, thermal decomposition by excess heat, contamination by impurities, account for the instability of biodiesel (Pambou-Tobi *et. al.*, 2010, Melton *et. al.*, 1994). The major biodiesel stability problem is oxidation instability. Oxidation instability affects biodiesel primarily during a long period of storage without use.

Oxidation of biodiesel is mainly due to unsaturation in its fatty acid chains; the presence of double bonds in its molecule offers a high level of reactivity with oxygen, especially when it is in contact with air or water (Su and White, 2004; Watkins *et. al.*, 2004). The primary oxidation products of double bonds are unstable allylic hydro-peroxides which easily form a variety of secondary oxidation products (Jain and Sharma, 2010; Sarin *et al.*, 2007). The hydro-peroxides formed may polymerize with other free radicals to form insoluble sediments, which can result into fuel filter plugging and deposits in the combustion chamber and injection system (Jain and Sharma, 2010; Lamers, 2010; Chen *et. al.*, 2009).

Biodiesel oxidation instability caused due to poor storage conditions is traceable to exposure to air, light, heat, high temperature and direct contact with certain metals (Choe and Min, 2007; Dana, 2003; Natarajan, 2012). These environmental factors promote biodiesel degradation reactions such as hydrolytic, photolytic and thermolytic reactions (Arora, 2009; Dunn, 2008; Dunn, 2009).

Prevention of biodiesel oxidation instability during storage demands urgent and crucial attention in ensuring the viability and sustainability of biodiesel. Hence, the focus of this research is to investigate the oxidation stability of biodiesel produced from waste groundnut oil under three different storage environmental conditions by considering its physico-chemical properties.

2.0 Methodology

2.1 Preparation of Hanous solution: 18.6g of Iodine crystals was weighed and added to 1L of glacial acetic acid solution and warmed to dissolve. 3ml of bromine water was also added to the mixture placed in a standard flask shook thoroughly to form Hanous solution and then placed in the fume cupboard.

2.2 Preparation of 15% Potassium Iodide solution: 15g KI was dissolved in 85g distilled water to obtain 15%w/w solution. The solution was well shaken and placed in a 250ml standard flask.

2.3 Preparation of standard sodium thiosulphate solution ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$): 25g of sodium thiosulphate was dissolved in 1 litre of freshly boiled distilled water; solution stability was improved by adding 0.1 g of Na_2CO_3 and 0.5 ml of chloroform (CHCl_3) was added as preservative to prevent growth of thiobacillus thioparus. The solution was stored in a clean glass bottle in the dark.

2.4 Preparation of 0.5M alcoholic potassium hydroxide solution: 30 grams of KOH pellets was added to 30ml of distilled water and then diluted to 1litre of ethanol to dissolve completely.

2.5 Biodiesel Production: Groundnut oil was filtered using industrial sieve of 80 μm pore diameter to remove impurities present in the oil. The oil was then heated to 110°C for 30 minutes to evaporate water present in the oil. The heated groundnut oil was then allowed to cool to 60°C. 100g of the warmed oil was weighed and kept in a 250ml beaker. In each experimental run, KOH catalyst was added to the required quantity of methanol and carefully agitated to ensure that KOH dissolved completely to form a methoxide solution.

The methoxide solution was gently added to the heated oil in a conical flask which was air tight with a thermometer used to monitor the temperature of the reaction. The experimental setup was placed on a magnetic stirrer to stir rigorously with the speed of 450rpm for 60 minutes at 60°C and the mixture was stirred vigorously. A mixture of the two products formed after the reaction was transferred into the separating funnel and allowed to settle for 6 hours by gravity. The top layer was a lighter coloured biodiesel and bottom product was a darker glycerin which was first drained off. Biodiesel obtained was free of impurity by washing repeatedly with warm water until no trace of impurity was found in the biodiesel. Then the wet biodiesel was heated to 110°C to remove trace of water present.

2.6 Experiments on the Stability of Biodiesel: Biodiesel produced was divided into three portions and subjected into three different environmental conditions for some days: a portion was stored in refrigerator at temperature of -20°C, another in a vacuum at temperature of 0°C and the third portion was exposed to the atmosphere ($T = 28^\circ\text{C}$). The following fuel properties that influence biodiesel oxidation stability were investigated on each of the biodiesel kept at three environmental conditions at different time interval.

2.6.1 Biodiesel Acid value determination: 95% ethanol was neutralised with dilute 0.1M NaOH solution. 5g of biodiesel was added to 50ml of the neutral ethanol and 50ml benzene. The mixture was shaken thoroughly and heated to 70°C for first bubbling. After cooling, the solution was titrated with 0.1M KOH solution, using phenolphthalein as indicator. The end point was the appearance of a pale pink colour.

2.6.2 Biodiesel Iodine value determination: 10ml of chloroform was added to 0.30g of the biodiesel in the conical flask and 25ml of ianous iodine solution (already prepared) was added to the content of the flask. The conical flask was enclosed with rubber corks and shook vigorously to ensure complete mixing and then placed in a very dark environment for over 30 minutes. After removing from dark room, 10ml of 15% of the prepared KI and 100ml of distilled water were added to the content. This was titrated against the prepared standardized sodium thiosulphate solution. Once a yellow colour is achieved during titration, 2 drops of starch indicator are added and the same thiosulphate solution was further used to titrate the solution until a colorless solution with a pink precipitate was obtained.

2.6.3 Biodiesel Saponification Value determination: 30g of KOH was added to 200ml of ethanol which was partially immersed in a bigger beaker containing cold water. The content was continuously stirred until KOH dissolved completely. 25ml of this solution was measured and added into 2g of biodiesel in conical flask. The content was put in a soxhlet apparatus which was placed in a water bath and heated to 70°C. After a period of 1 hour, the content of the flasks was cooled. It turned pink after 2 drops of phenolphthalein was added and then colorless after titrating against standard 0.1M HCl.

2.6.4 Biodiesel Viscosity determination: A U-tube viscometer was clamped on the retort stand and biodiesel sample was poured into the standard viscometer till it reached the mark. A pipette filler was used to suck up the biodiesel till it reached the upper mark and then a stopwatch was used to obtain the time taken for the sample to reach the lower mark level.

2.6.5 Biodiesel Peroxide value determination: 1g of biodiesel was weighed in the three conical flasks. A blank conical was also set at the same time. 1g of powdered KI was completely dissolved in a solution containing 100ml of glacial acetic acid and 50ml of chloroform. 20ml of the mixture was added to 1g of biodiesel sample. 0.002M of $\text{Na}_2\text{S}_2\text{O}_3$ solution was titrated against the solution until the yellow colour obtained disappeared. 0.5ml starch solution was then added to the solution and titrated again until the blue colour obtained disappeared.

3.0 Results and Discussion

Minitab 16 software, using factorial experimental design method, was adopted in the design of experiments. Reaction temperature of 60 °C and reaction time of 60 minutes were kept constant during the experiments. And the biodiesel yield obtained (at different catalyst concentration and methanol/oil mole ratio) were as shown in

Table1.

Table1: Biodiesel Yield obtained from Groundnut Oil Trans-esterification

Methanol/Oil mole ratio	Catalyst concentration (w/w% Oil)	Yield (%)
5.0	0.4	85.5
5.0	1.0	83.7
9.0	0.4	85.9
7.0	0.7	88.0
7.0	0.7	88.7
7.0	0.7	88.2
7.0	1.1	86.3
4.2	0.7	84.6
7.0	0.7	86.1
7.0	0.7	87.2
9.8	0.7	88.1
9.0	1.0	89.2
4.2	0.7	84.1

The results of the interactions of catalyst concentration, methanol/oil mole ratio and biodiesel yield were represented in Figure 1. Maximum biodiesel yield was obtained at the experimental conditions of methanol/oil mole ratio of 9 and catalyst concentration of 1.0w/w%Oil. That is, high yield was favoured by increase in methanol/oil mole ratio and increase in KOH catalyst concentration.

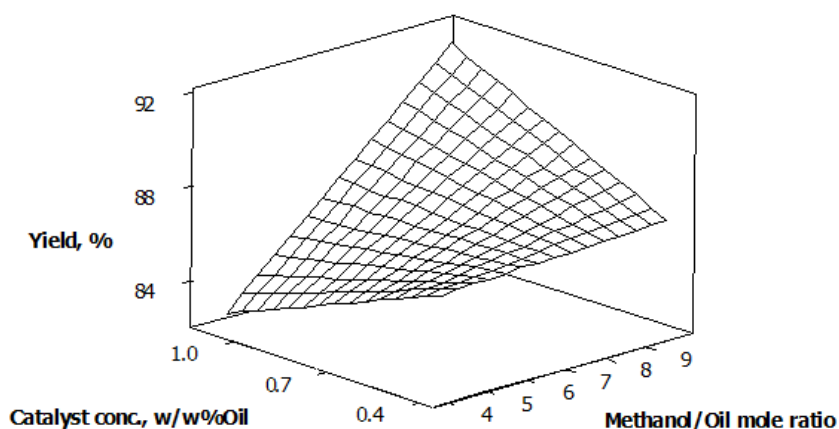


Figure 1: Biodiesel Yield obtained from Methanol/Oil mole ratio and Catalyst Concentration.

The physico-chemical properties of the biodiesel produced when subjected to three different storage conditions were as shown in Figure 2 – 6. Figure 2 shows the saponification values obtained during storage period of biodiesel at the three different environments. Saponification value is the number of mg of potassium hydroxide (KOH) required to neutralise the free acids in the biodiesel. An increase in saponification values of biodiesel is an indication of the increase in free fatty acids with time, due to oxidation reactions. The same reasons accounted for the similar results obtained in Figures 3 and 4. The higher the peroxide values, the higher the rate of peroxide formation. This is because peroxide value measures the oxidation progression and the formation of secondary oxidation products (Dunn, 2009).

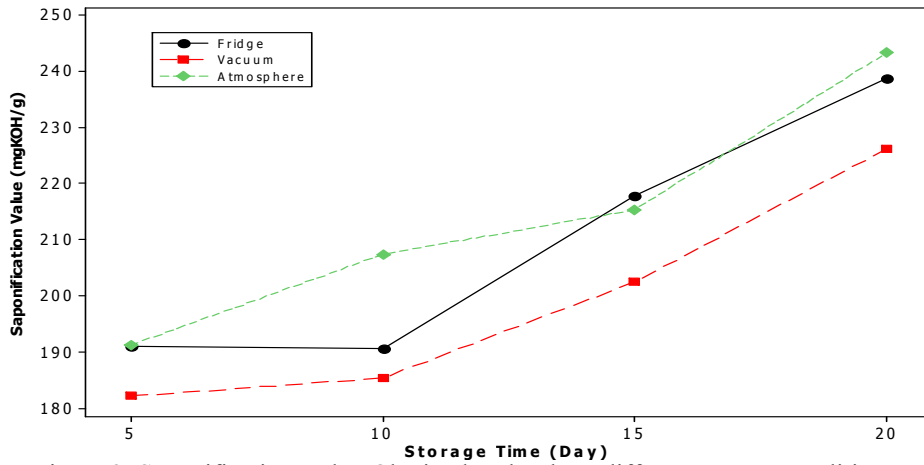


Figure 2: Saponification Value Obtained under three different storage conditions

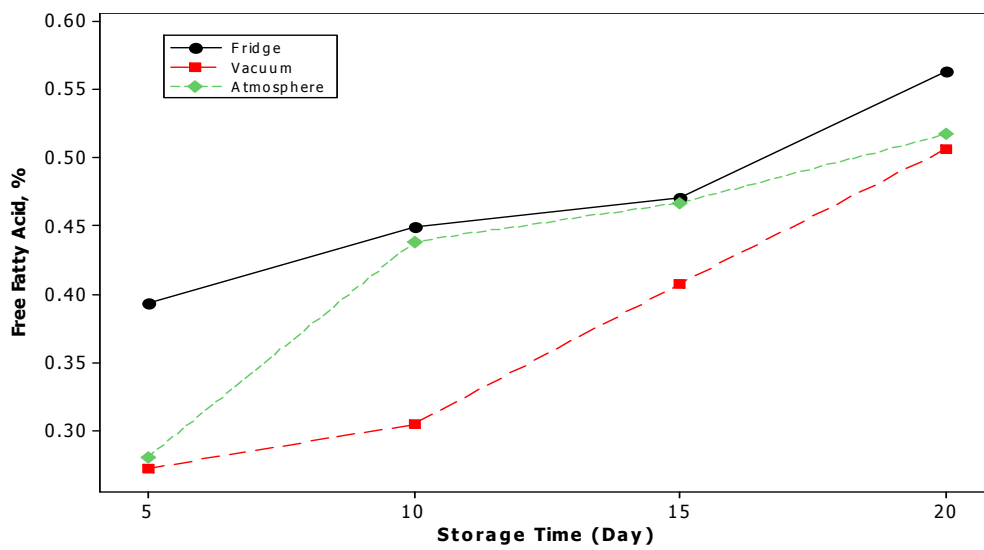


Figure 3: Free Fatty Acid Obtained under three different storage conditions

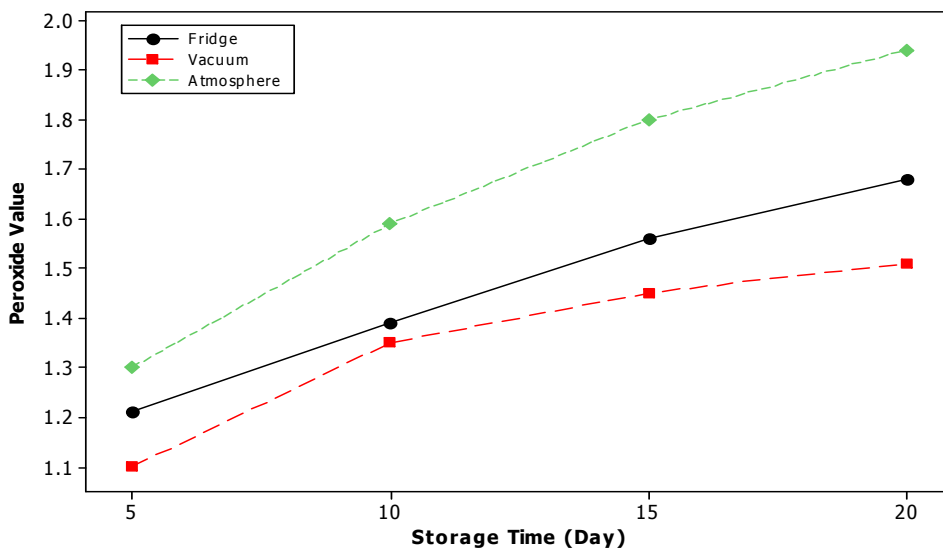


Figure 4: Free Fatty Acid Obtained under three different storage conditions

In Figure 5, decrease in iodine value (a measure of the level of unsaturation in organic compounds) results from reduction in the degrees of unsaturation of biodiesel with time. The oxidation reactions converted certain degree of unsaturated fatty acids of biodiesel to saturated fatty acids. Also, it is observed that the rate of reduction in IV

varied, depending on the storage condition. Biodiesel exposed to the atmosphere recorded highest rate of reduction while biodiesel stored in the vacuum experienced least rate of IV reduction.

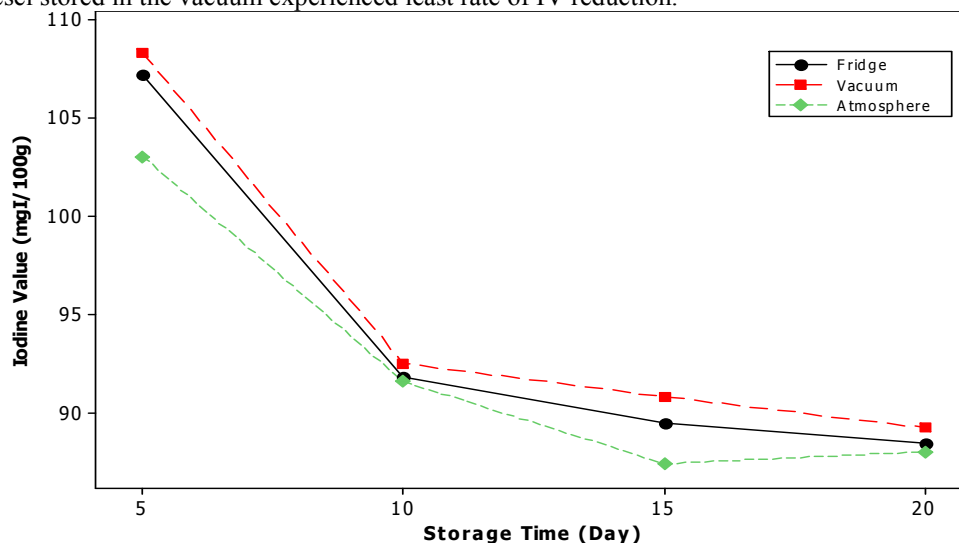


Figure 5: Iodine Value Obtained under three different storage conditions

Figure 6 reveals that biodiesel becomes less viscous as a result of oxidation reactions which it undergoes during storage. Vacuum condition gave the least rate of viscosity by imposing highest resistance to oxidation reaction, while the atmospheric condition favoured high rate of biodiesel viscosity.

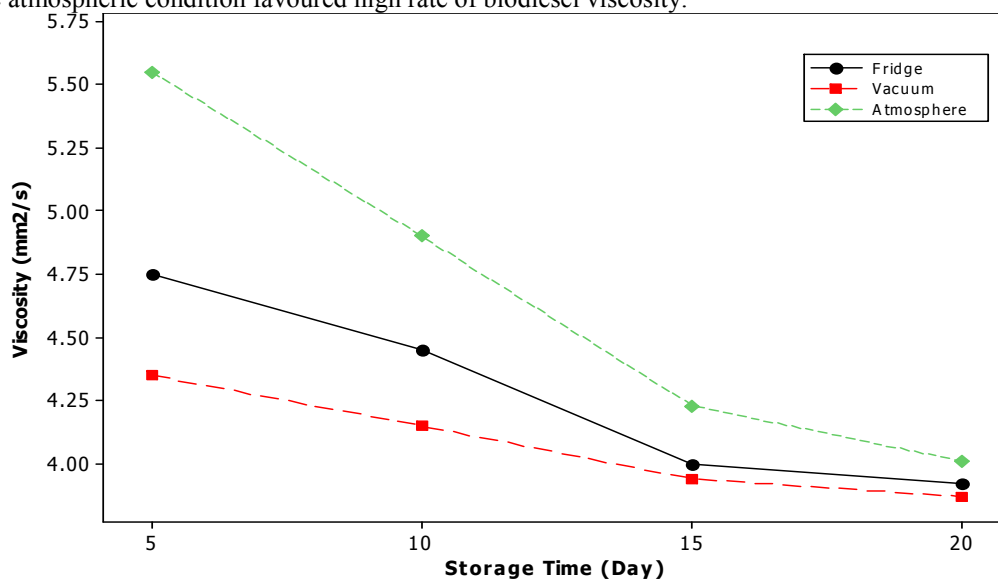


Figure 6: Viscosity Obtained under three different storage conditions

4. Conclusion

The results of the experiments show that one of the factors affecting biodiesel stability is oxidation reactions due to the presence of moisture, heat and light. And that vacuum is the most favourable condition (compared to freezing and atmospheric conditions) for the storage of biodiesel.

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