Enhancement of Shelf-Life and Oxidative stability of *Jatropha curcas* Biodiesel in Zimbabwe

[1]C.S. Shonhiwa-*University of Zimbabwe Faculty of Engineering Mechanical Department*

[2]R.L.M. Nhamo-*University of Zimbabwe Faculty of Science Chemistry Department and*

[3]J. Kugara *University of Zimbabwe Faculty of Science Chemistry Department*

Abstract

Biodiesel is an environment friendly liquid biofuel similar to petro-diesel in terms of fuel quality and combustion characteristics. Increasing environmental concerns, fast depleting petroleum reserves and agriculture based economy of Zimbabwe are the driving forces to promote biodiesel as an alternative renewable fuel. Biodiesel, derived from *Jatropha curcas* seed oil has great potential to be used as a diesel engine fuel in Zimbabwe to reduce air pollution and to reduce dependence on limited fossil fuel.

Under normal storage conditions diesel fuel can be expected to stay for 12 months or more at 20^{o}C. The research carried out showed that the Jatropha biodiesel has a storage life of 3 months. Beyond this period, the diesel reacts with oxygen from the atmosphere that forms fine sediments and gums, which block the fuel filters leading to poor performance of the engine. This is attributed to the presence of double bonds in the *J. curcas* oil mainly oleic, linoleic or linolenic acids. *J. curcas* biodiesels have different amounts of esters (which vary from different geographical location) and the trend of increasing stability is linolenic < linoleic < oleic. These esters undergo auto-oxidation with different rates depending upon the numbers and positions of the double bonds and result in the formation of a series of by-products like acids, esters, aldehydes, ketones, lactones among others. Therefore the aim of the current work is to study the oxidation stability of *J. curcas* biodiesel and also the effectiveness of various antioxidants which enhance its shelf life. Five antioxidants namely tertiary Butylhydroquinone (TBHQ), Butylated hydroxytoluene (BHT), Butylated hydoxanisole (BHA), Pyrogallol (PY) and Gallic Acid (GA) have been used in this work. PY was found to be the best antioxidants among all 5 antioxidants used. The optimum amount of antioxidant (PY) for pure biodiesel was 3000 ppm.

Keywords

Antioxidant, shelf-life, oxidative stability,Jatropha curcas oil

1.0. INTRODUCTION

Biodiesel, defined as fatty acid mono-alkyl esters is made from domestically renewable feedstock such as *Jatropha* seed oil. It is an alternative fuel, which is environmentally innocuous for combustion in compression–ignition (diesel) engines. It is relatively safe to handle (high flash points), and has an energy content, specific gravity, kinematic viscosity (KV) and cetane number (CN) comparable to those properties of petro diesel (1,2).

Zimbabwe with an estimated annual consumption of 1 billion liters diesel consumption is all of which is imported has become a fast growing renewable liquid biofuel promoter in the Africa. The main challenge of biofuels is that they undergo degradation over time, mainly influenced by temperature and oxygen. Degradation products of biodiesel such as insoluble gums and sediments, or the formation of organic acids and aldehyde may cause engine and injection problems (2-3).

Jatropha biodiesel properties degrade during long-term storage as follows: (i) oxidation or autoxidation from contact with ambient air (ii) thermal-oxidative decomposition from excess heat (iii) hydrolysis from contact with water or moisture in tanks and fuel lines or (iv) microbial contamination from migration of dust particles or water droplets containing bacteria or fungi into the fuel. The effects of autoxidation on biodiesel fuel quality during long-term storage presents a significant concern for biodiesel producers, suppliers, and consumers (4). Therefore engine and injection pump producers insisted on the parameter of oxidation stability which was fixed at a minimum limit of a 6-hour induction period at 110^0C (4, 5).

The method adopted for determination of the oxidation stability in this research work is called Rancimat method which is commonly used in the vegetable oil sector. The literature review has revealed that high contents of unsaturated fatty acids, which are very sensitive to oxidative degradation, lead to very low values for the induction period.

Several studies showed that the quality of biodiesel over a longer period of storage strongly depends on the tank material as well as on contact to air or light. To enhance oxidative stability and to guarantee a prolonged shelf life of biodiesel, it will be necessary to find appropriate additives and its dosage for the biodiesel produced.

Researchers have evaluated the beneficial effects of the antioxidant additive tertiary butylhydroxyquinone (TBHQ) on sunflower oil methyl and ethyl ester stability (6). Similar results on soybean oil methyl esters were observed by Dunn using TBHQ and a tocopherol, even under accelerated conditions (7).

Although there are numerous publications on the effect of natural and synthetic antioxidants on the stability of oils and fats used as food and feed, little is available on the effect of antioxidants on the behavior of as Jatropha biodiesel from the *Jatropha curcas* species being grown in Zimbabwe. Simkovsky, et al. studied the effect of different antioxidants on the induction period of rapeseed oil methyl esters at different temperatures but did not find any significant improvements (8). Canakci, et al. tested the influence of the antioxidant TBHQ on the PV of soybean oil methyl esters during storage and found good improvement of stability. Acid value and kinematic viscosity however are two important parameters for rapid assessment of biodiesel fuel quality as they continuously increase with deteriorating fuel quality.

The aim of the present study is to enhance the shelf life and oxidative stability of biodiesel from the *J. curcas* species being grown in Zimbabwe.

2.0. OBJECTIVES

To retard oxidative degradation and guarantee a specific stability of Jatropha curcas biodiesel by use of a synthetic appropriate antioxidant.

3.0. METHODOLOGY

Rancimat tests for oxidation stability were used in this study. Using different antioxidants in different concentrations, the fuel properties such as Acid value (AV), Peroxide value (PV) and

Kinematic viscosity (KV) of Jatropha Bio-Diesel were determined at regular intervals of time for 12 months.

Jatropha curcas oil used for the study was produced from fresh seeds purchased from Mutoko and Mudzi districts in Mashonaland East Province. Analytical Grade Methanol and catalyst Sodium hydroxide were supplied by the Chemistry Department at University of Zimbabwe. Jatropha bio-diesel were prepared in Chemistry laboratory at University of Zimbabwe and characterized as indicated in the following table 1.

Table 1. Characteristics of Jatropha curcas oil and biodiesel from Mashonaland East Province

Fatty Acid Composition (%)	**Myristic**	**Palmitic**	**Staeric**
	0.43	14.81	6.79
	Oleic	**Linoleic**	**Linolenic**
	45.20	31.54	0.82
Physical Property		**Jatropha Oil**	**Jatropha Biodiesel**
Kinematic Viscosity @ 38^{o}C (cSt)		32.67	4.91
Density @ 15^{o}C		0.882	0.873
Cloud Point(^{o}C)		9	4
Pour Point(^{o}C)		3	1
Flash Point(^{o}C)		229.3	198.9
Acidity(mgof KOH/g)		32.8	0.46

3.1. Storage condition

All the biodiesel samples of volume 200 ml were stored in open glass bottles of 250 ml capacity and kept in doors, at a room temperature of 30^{0} C. The samples were exposed to air as well as daylight conditions. The containers were fully opened for them to be incontact with air. Every week 54 samples were taken for analysis of Peroxide value, Kinematic viscosity and Acid value. Each sample was repeated three times for the determination of average value.

3.2. Determination of Peroxide Value (PV)

The peroxide value was determined by measuring the amount of iodine which was formed by the reaction of peroxides (formed in biodiesel) with iodide ion.

$2\ I^{-} + H_2O + HOOH \rightarrow HOH + 2OH^{-} + I_2$

Note that the base produced in this reaction was taken up by the excess of acetic acid present. The iodine liberated is titrated with sodium thiosulphate.

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$

3.2.1. Reagents and solutions

1. Acetic Acid - chloroform solution (7.2ml Acetic Acid and 4.8ml Chloroform).

2. Saturated Potassium Iodide solution. Store in the dark.

3. Sodium thiosulfate solution, 0.1N. Commercially available.

4. 1% Starch solution. Commercially available.

5. Distilled or deionized water.

3.2.2. Procedure

1.5.00 (±0.02)g of sample were weighed and put into a 100 ml glass stoppered Erlenmeyer flask. Record weight to the nearest 0.01g.

2. By using graduated cylinder, 30 ml of the acetic acid - chloroform solution were added.

3. The flask was swirled until the sample was completely dissolved (careful warming on a hot plate may be necessary).

4. By using 1 ml Mohr pipette, 0.2 ml of saturated potassium iodide solution were added

5. The flask and the contents were swirled for exactly one minute.

6. Immediately 30 ml of either distilled were added, stoppered and shaked vigorously to liberate the iodine from the chloroform layer.

7.0.01M sodium thiosulfate were filled in a burette and titrated using starch solution as indicator.

3.2.3. Calculation Models

Peroxide Values (PV) was calculated using equation given by Maisuthisakul and Charuchongkolwongs.

$$PV = \frac{(V_s - V_b)NF}{W} \times 100 \quad (1)$$

PV is peroxide value of biodiesel sample measured in milliequivalent of peroxide per kg of biodiesel sample,

V_s is Volume of sodium thiosulphate solution (ml) used for neutralization,

V_b is Volume of sodium thiosulphate solution used for neutralization for blank test determined as 2.8ml, W is weight of biodiesel sample measured (g),

F is the factor from standardization with Potassium Iodide

N is normality of sodium thiosulphate solution (0.01 M).

Oxidative stability (S) is evaluated from peroxide values as thus:

$$S = \frac{(PV_i - PV_j)}{PV_j} \times 100 \quad (2)$$

S is the oxidative stability measured in percent,

PV_i is the peroxide value of biodiesel sample with antioxidant,

PV_j is the peroxide value of biodiesel sample without antioxidants.

Continues titrating for at an interval of one week for six months.

3.3. Determination of oxidative stability

Oxidative stability (OS) of Jatropha biodiesel sample was studied with a Rancimat instrument . In the Rancimat procedure the sample was heated at a constant temperature with an excess airflow, which passed through a conductivity cell filled with distilled water. During this oxidation process volatile acids are formed and the conductivity increases at an end and the period up to this point is called ‘‘Induction period”. The induction period of *Jatropha curcas* biodiesel was determined without antioxidant and with different antioxidants (BHA, BHT, TBHQ, PY and GA) and under different concentrations of the antioxidants (500, 1000, 2000 & 3000ppm) at 30^0C.

3.4. Evaluation of Storage stability

To evaluate the storage stability the KV and AV values were determined at 25^0C and 30^0C over a period of 50 weeks at regular intervals of one week.

4. 0. Results

Table 2 shows the induction period of Jatropha biodiesel using different antioxidants at different concentration.

Table 2. Induction time of Jatropha curcas biodiesel with different antioxidants and at different concentrations.

Antioxidant	Without antioxidant (hours)	Induction Time (Hours)			
		500ppm	1000ppm	2000ppm	3000ppm
BHA	2.0	3.1	3.6	4.7	6.8
BHT	2.0	3.2	4.0	5.5	7.0
GA	2.0	2.2	2.9	3.1	3.3
TBHQ	2.0	2.3	2.8	6.3	11.8
PY	2.0	3.6	6.6	15.7	18.6

The study reveals Pyrogallol (PY) to be the best antioxidant which showed the best improvement in the OS of Jatropha biodiesel that is 18.6 h at a concentration of 3000 ppm at 30^0C. The study also reveals that with TBHQ the Oxidation stability of biodiesel is enhanced to 11.8 h at a concentration of 3000 ppm at 30^0C. All the other antioxidants used have small improvement in the induction period.

4.2. Evaluation of Storage Stability

4.2.1. Kinematic Viscosity (KV)

During storage, the viscosity of the methyl esters increases by the formation of more polar, oxygen containing molecules and also by the formation of oxidized polymeric compounds that can lead to the formation of gums and sediments that clog filters. The kinematic viscosity of Jatropha biodiesel at the initial stage at 30^0C was 8.4 cP. When the biodiesel was left by itself for duration of 1 year in an open to air and light condition, the oxidation process started and the KV value rose enormously to a high value of 18.4 cP which is an indication that storage stability of biodiesel is a serious problem.

Table 3. Kinematic Value and Acid Value at 30° C

WK	Without		With Antioxidant		Antioxidant Conc. (ppm)	Week 10		Week 20		Week 30		Week 40		Week 50	
	KV (cP)	AV (mg KOH/g)				KV (cP)	AV (mgKOH/g)	KV (cP)	AV (mgKOH/g)	KV (cP)	AV (mg KOH/g)	KV (cP)	AV (mgKOH/g)	KV (cP)	AV (mg KOH/g)
0	8.4	0.4	1	BHT	3000	9.6	1.2	10.3	1.9	11.8	2.6	13.0	3.4	14.3	4.2
					2000	9.5	1.1	10.5	1.6	11.4	2.4	12.4	3.0	13.5	3.7
					1000	9.4	1.0	10.8	1.4	11.2	2.0	12.2	2.6	13.0	3.2
					500	9.3	0.9	10.9	1.5	10.5	1.8	11.3	2.3	12.0	2.7
10	9.0	1.2	2	BHA	3000	9.3	1.2	10.4	2.0	11.5	2.8	12.5	3.6	13.6	4.5
					2000	9.1	1.0	10.1	1.6	10.9	2.2	11.8	2.8	12.7	3.4
					1000	9.0	0.9	9.7	1.4	10.4	1.8	11.0	2.4	11.7	2.9
					500	8.9	0.9	9.3	1.2	9.9	1.6	10.4	2.0	10.9	2.4
20	12.6	3.6	3	GA	3000	9.5	1.2	10.3	1.9	11.3	2.7	12.3	3.5	13.3	4.3
					2000	9.4	1.0	10.2	1.7	11.2	2.4	12.2	3.0	13.1	3.8
					1000	9.1	0.9	9.8	1.4	11.5	1.9	11.3	2.4	13.0	2.9
					500	8.9	0.8	9.6	1.2	10.3	1.7	10.9	2.0	11.7	2.5
30	14.8	5.5	4	TBHQ	3000	9.3	1.3	10.5	2.3	11.7	3.2	12.8	4.2	14.0	5.1
					2000	9.2	1.1	10.3	1.8	11.4	2.6	12.4	3.4	13.4	4.2
					1000	9.0	1.0	9.6	1.6	10.2	2.2	10.8	2.8	11.5	3.4
					500	8.9	0.8	9.3	1.3	9.8	1.7	10.3	2.2	10.7	2.6
40	16.6	6.9	5	PY	3000	9.3	1.1	10.4	1.9	11.5	2.6	12.5	3.4	13.6	4.1
					2000	9.2	1.0	10.2	1.7	11.2	2.3	12.2	3.0	13.1	3.7
					1000	9.0	0.9	9.8	1.5	10.8	2.0	11.4	2.5	12.2	3.1
50	18.4	7.2			500	8.8	0.8	9.5	1.3	10.2	1.7	10.8	2.2	11.5	2.6

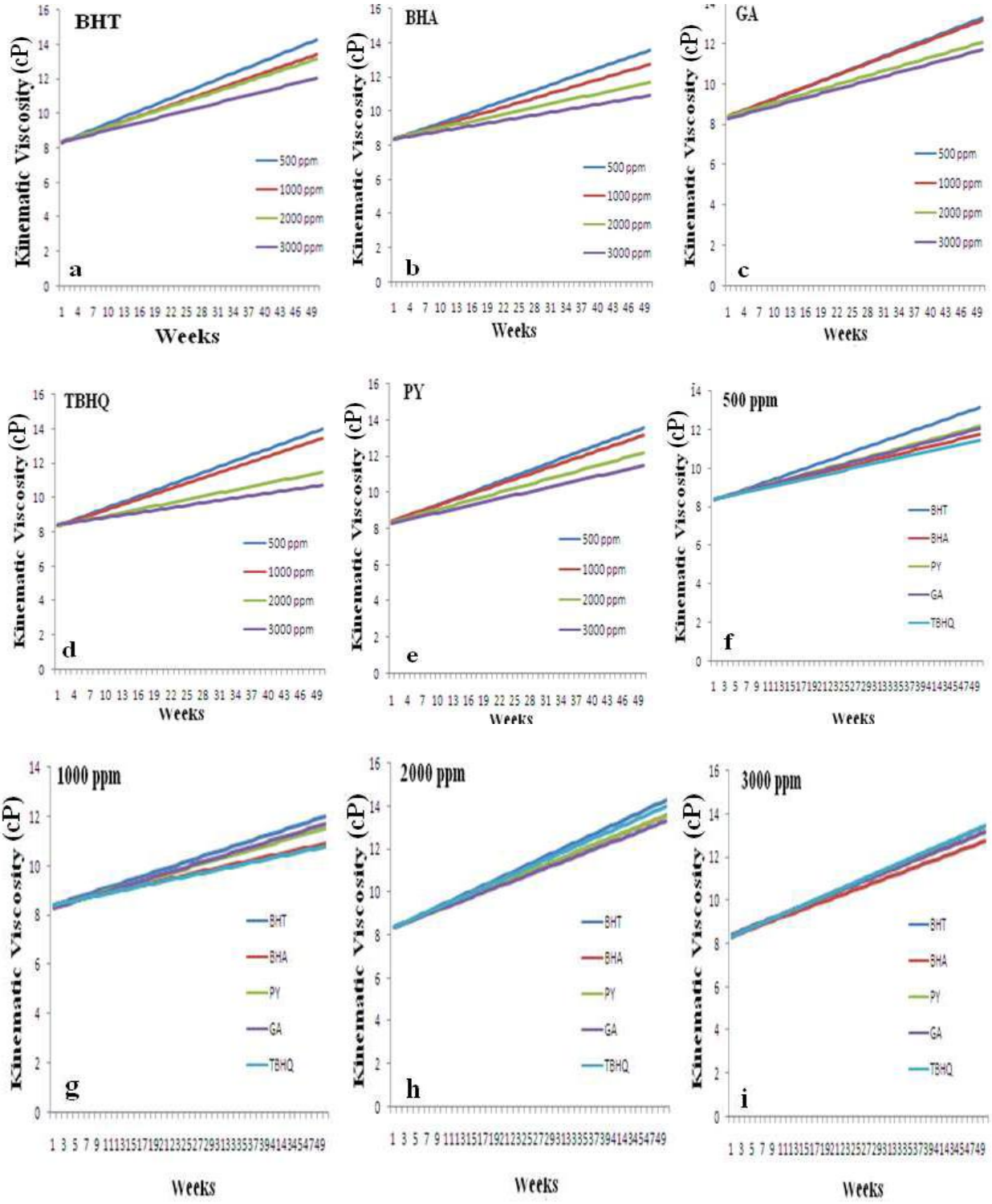

Fig. 1. Change of Kinematic viscosity of JBD with time. Figure (a to e) indicate the variation of kinematic viscosity with different antioxidants at different concentrations. Fig (f to i) indicate the variation of kinematic viscosity with different antioxidants at a particular concentration of antioxidant.

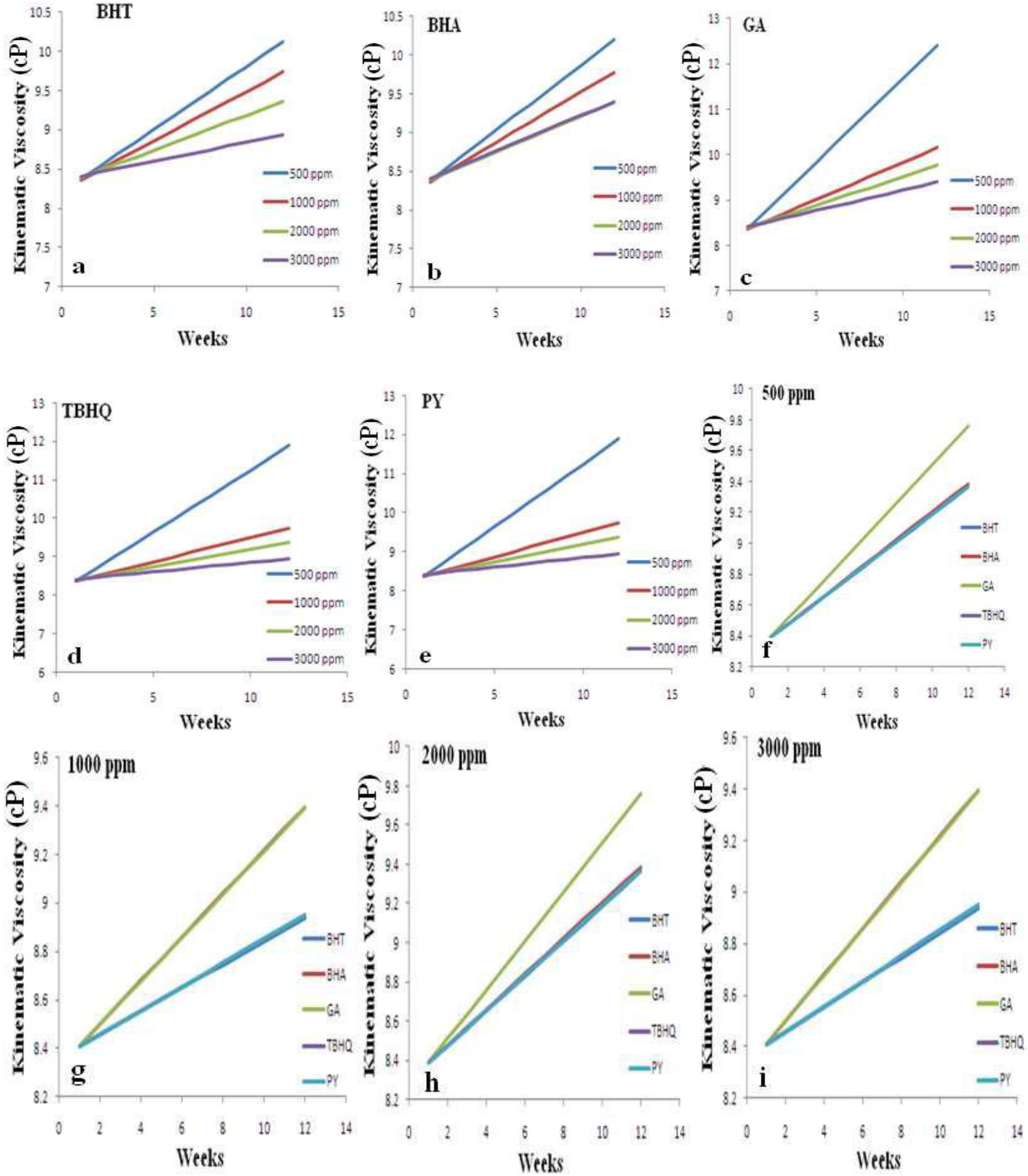

Figure 2: Change of Kinematic viscosity of JBD with time. Fig (a to e) indicate the variation of kinematic viscosity with different antioxidants at different concentrations. Figure (f to i) indicate the variation of kinematic viscosity with different antioxidants at a particular concentration of antioxidant.

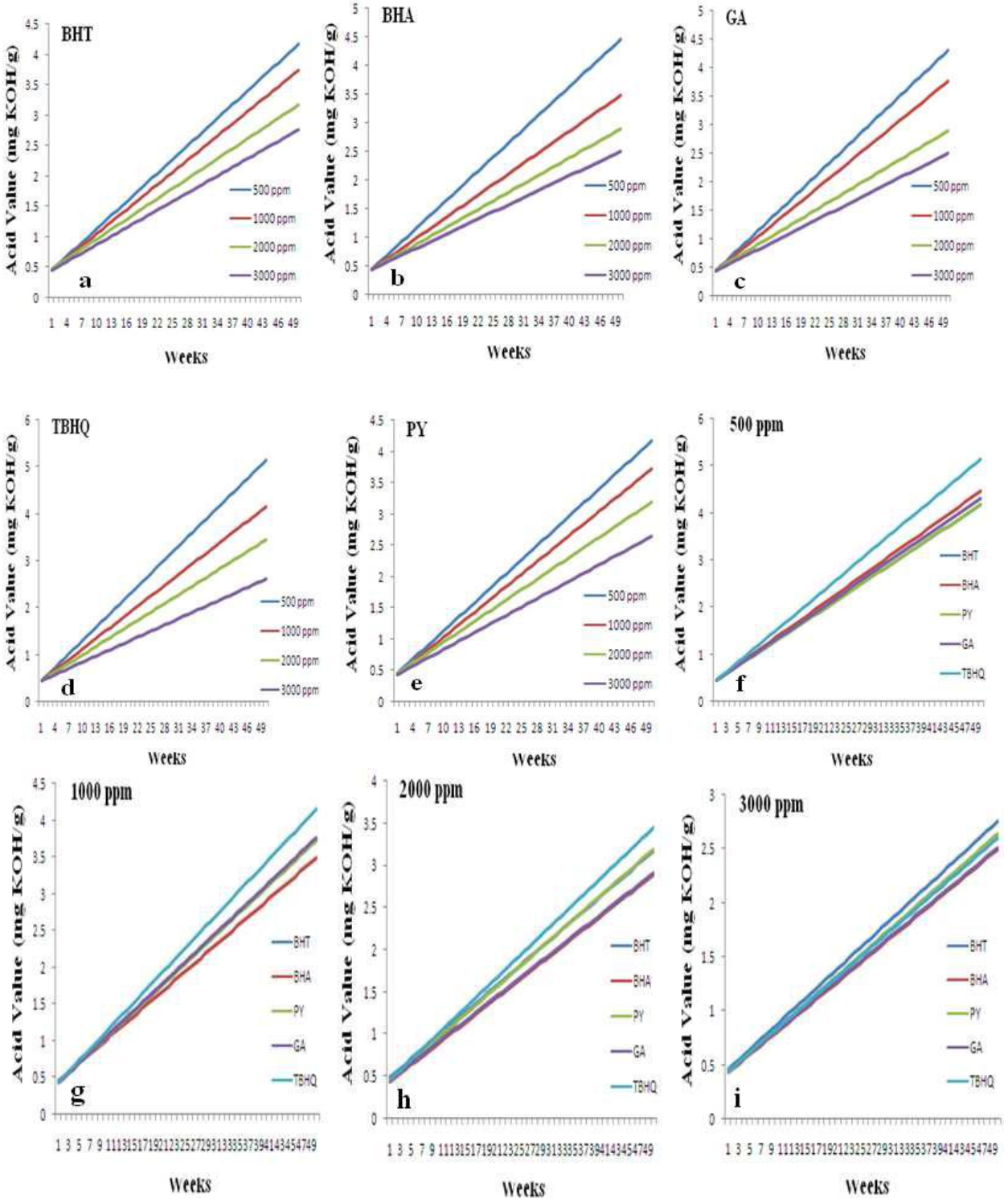

Figure 3: Change of Acid value viscosity of JBD with time. Figure a to e indicate the variation of Acid value with different antioxidants at different concentrations. Figure f to i indicate the variation of Acid value with different antioxidants at a particular concentration of antioxidant.

On employing antioxidants to retard the oxidation process during storage it is found that the antioxidants definitely improve the storage stability (Table 3). All the five antioxidants tested showed that at a concentration of 3000 ppm, they are able to substantially retard the oxidation process during a one year storage period at 30^0C and improve the storage stability of the biodiesel. Antioxidants BHA and TBHQ seem to have a better effect on the storage stability of Jatropha Biodiesel than the other antioxidants over a 50 week period at a concentration of 3000 ppm

4.3. Acid Value (AV)

The acid value (AV) of Jatropha biodiesel samples also increased with increasing storage time as a result of hydrolysis of fatty acids methyl esters to fatty acids . The acid value of Jatropha biodiesel initially was 0.4 mgKOH/g. when the biodiesel was stored in an open to air condition and kept for 50 weeks it was found to undergo oxidation and the AV rise up to a very high value of 7.2 mg KOH/g. From table 3, it is evident that the addition of antioxidants to retard the oxidation is found to be effective with all the five antioxidants when the antioxidants concentration is 3000 ppm. At a concentration of 500 ppm, PY is found to be the best antioxidant. Similarly at a concentration of 3000 ppm BHA is shown to be the best antioxidant.

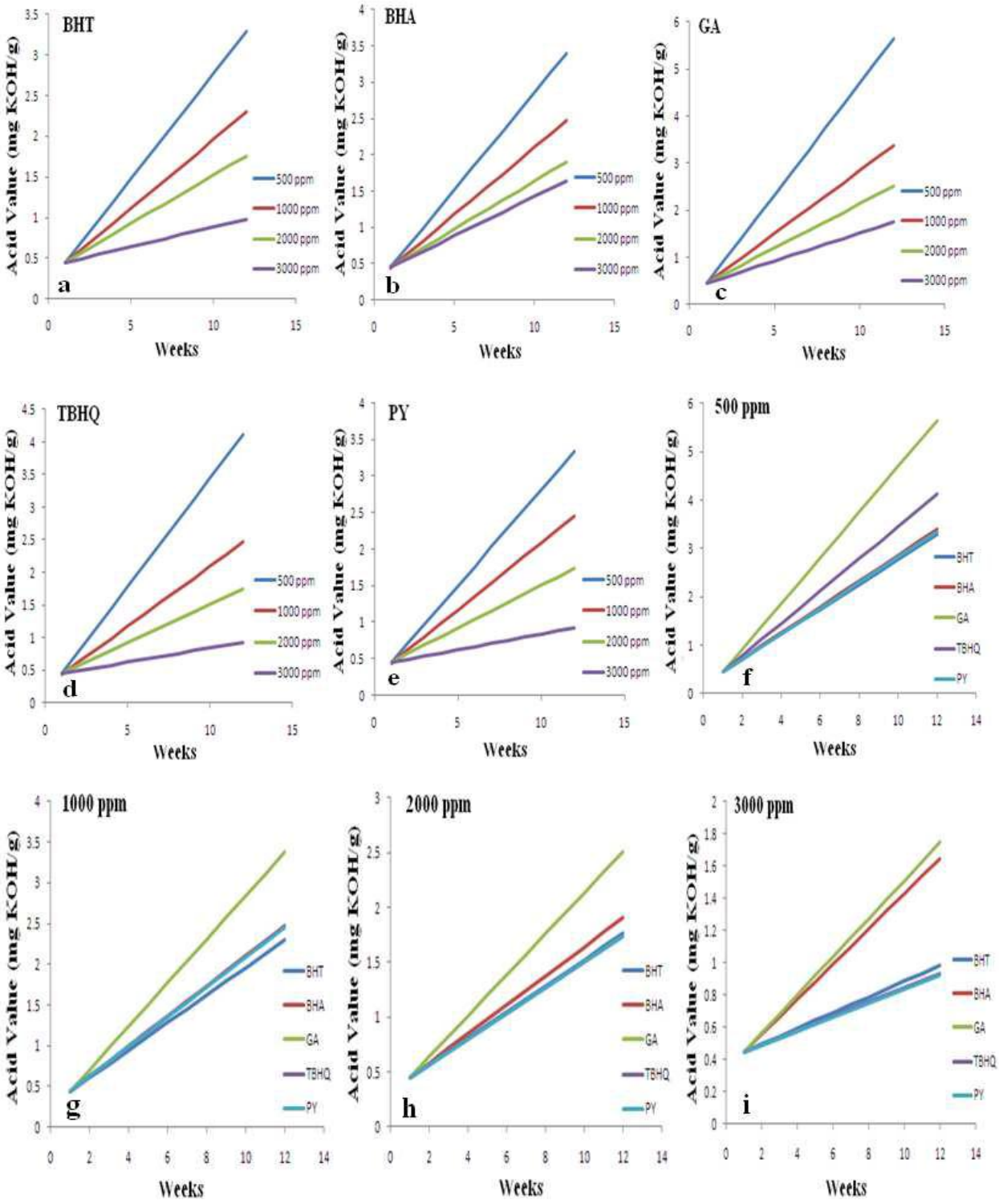

Figure 4: Change of Acid value of JBD with time. Figure a to e indicate the variation of acid value with different antioxidants at different concentrations. Fig f to i indicate the variation of acid value with different antioxidants at a particular concentration of antioxidant.

5.0 CONCLUSIONS

The effect of Pyrogallol as an antioxidant for Jatropha biodiesel is found to be the best as it increased the induction time from 2.0 h to 18.6 h, when the concentration of pyrogallol was 3000 ppm. KV and AV values are good indicators of storage stability of biodiesel. They increase on increase of storage time. A concentration of 3000 ppm of antioxidants like BHT, TBHQ, PY, GA, and BHA has a beneficial effect on the storage stability of Jatropha biodiesel.

6.0. RECOMMENDATIONS

In order to minimize potential negative effects on diesel engine vehicles, it is recommended to use a minimum of 3000ppm of antioxidant pyrogallol.

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7.0. References

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