Australian Journal of Basic and Applied Sciences, 11(3) Special 2017, Pages: 187-191

AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

The Effect of Antioxidant on the Stability of Biodiesel from Grease Trap Oil

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ARTICLE INFO

Article history:
Received 18 September 2016
Accepted 21 January 2017
Available online 26 January 2017

Keywords:
Biodiesel Oxidation stability
Antioxidants Peroxide value
Acid Value

ABSTRACT

Biodiesel is renewable fuel and when blended with conventional petroleum diesel, biodiesel reduces hydrocarbon, particulate and carbon monoxide emissions while simultaneously improves lubricity, lowers sulfur, and has a high cetane number. Biodiesel from grease trap oil degrades due to oxidation, contact with water, and/or microbial activity. To avoid oxidation and extend the shelf life of biodiesel, commercial antioxidants can be added. **Objective:** In this study, butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), tertiarybutylhydroquinone (TBHQ) and propyl gallate (PG) were evaluated for their potential to reduce the degree of oxidation of biodiesel under normal temperature and humidity condition. Each antioxidant combination was added at a concentration between 250 to 1000 ppm. The oxidative stability was investigated and ASTM D6751-11 standard were used to monitor the changes using peroxide values (PV) and total acid number (TAN). For PV content, the effect of different antioxidants on biodiesel is as follow: 500 ppm PG, TBHQ-PG combination and TBHQ gave the best result. For TAN content, samples with antioxidants 500 ppm PG gave the best result followed by TBHQ and TBHQ-BHT. All grease trap oil based biodiesel samples with these antioxidants did not show any significant increase of PV and TAN values after 12 weeks storage compared to the untreated grease trap oil based biodiesel.

INTRODUCTION

Biodiesel aging and oxidation can lead to high acid numbers, high viscosity, and the formation of gums and sediments that clog filters. If the oxidation stability, acid number, viscosity, or sediment measurements exceed the limits in ASTM D6751 (2011), the Biodiesel (B100) is degraded to the point where it is out of specification and should not be used. Biodiesel with high oxidation stability will take longer than biodiesel with low oxidation stability to reach an out-of-specification condition. Monitoring the acid number and peroxide value over time can indicate whether it is oxidizing. Oxidation of oils such as biodiesel and conventional diesel probably occurs largely at the air-water interface (Frankel *et al*., 1994). Biodiesel should be tested at receipt to ensure that it is within specification (Tyson *et al*., 2006).

Pretreatment needs to stabilize and maintain the quality of biodiesel achieve by applying anti oxidizing agent to biodiesel. This method is widely used as chemical controls are easy to apply and effective to solve the problem. Many factors can affect oxidation of biodiesel such as microbial contamination, chemical contamination, exposure to light, temperature, exposure to air, type of feedstock and additives. Oxidation of oils such as biodiesel and conventional diesel probably occurs largely at the air-water interface (Frankel *et al*., 1994).

Previous studies have found that antioxidants can be effective in increasing the stability of biodiesel. However, these effects have not been fully elucidated and results have been inconclusive or conflicting. (Sendzikiene *et al*., 2005) found that butylated hydroxyanisole (BHA) and butyl-4-hydroxytoluene (BHT) have

To Cite This Article: Shaharuddin H., Wan Asma I., Zulkafli H., Nur Atiqah M. S., The Effect of Antioxidant on the Stability of Biodiesel from Grease Trap Oil. ***Aust. J. Basic & Appl. Sci.,*** *11(3): 187-191, 2017*

nearly the same effect on the oxidative stability of rapeseed oil-, and tallow-based biodiesel, and the optimal level of synthetic antioxidants was determined to be 400 ppm. (Mittelbac *et al*., 2003) reported that pyrogallol (PY), propylgallate (PG), and t-butylhydroquinone (TBHQ) could significantly improve the stability of biodiesel obtained from rapeseed oil, used frying oil, and beef tallow, whereas BHT was not very effective. The objective of the research is to study the effect of different anti-oxidant addition on the stability of biodiesel produced from high free fatty acid (FFA) content of grease trap oil.

MATERIALS AND METHODS

Materials:

The antioxidants namely butylated hydroxyanisole (BHA, 98.5%), butyl-4-methylphenol (BHT, 97%), 2, 5-Di-tert-butyl butylhydroquinone (TBHQ, 99%), and Prophyl gallate (PG, 98%) were purchased from Sigma-Aldrich Inc. The grease trap oil were obtained from a local contractor and the biodiesel B100 (100% biodiesel) was produced by a three stage method viz., pre-treatment, alkali catalyzed transesterification and post treatment (to remove un-reacted oil and glycerol) (Venkanna *et al*., 2009). The reagents and solvents were supplied by Merck and Fisher (Analytical Grade).

Methods:

Synthesis of biodiesel stage 1: Pre-treatment process (acid esterification):

The grease trap oil was esterified to triglycerides in a pre-treatment process with methanol using anhydrous H_2SO_4 (acid catalyst). The reaction was conducted at 60 ± 5 ºC for 60 min. After this time, the mixture was poured into a separatory funnel, where the excess methanol along with impurities moved to the top layer and was removed. The bottom layer was used for the alkali transesterification.

Synthesis of biodiesel stage 2: Alkali catalyzed transesterification process:

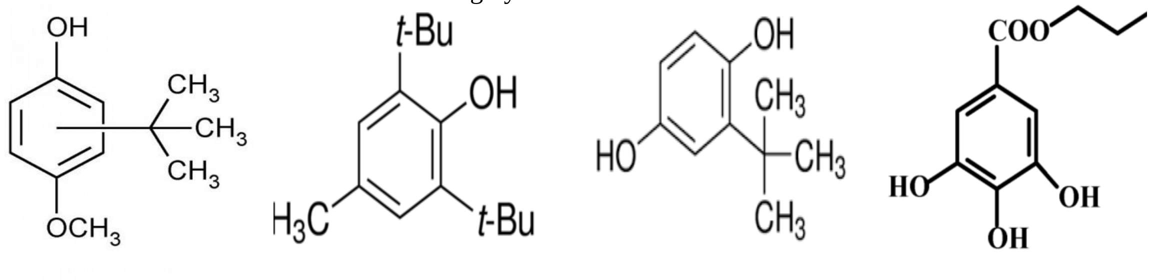
The bottom layer product of acid esterification was heated to the desired temperature before being synthesized by the catalytic transesterification using methanol as aliphatic alcohol and KOH as base (Almeida *et al*. 2011) The mixture was heated under reflux at 60 ± 5º C for 60 min. After this time, the mixture was poured into a separatory funnel and the product was allowed to settle under gravity for 12 h in a separating funnel. The products of the alkali transesterification process result in the formation of two layers viz., an upper layer containing a mixture of small quantities of unreacted oil, glycerol and transesterified products (esters) and a lower layer of glycerol. The lower layer of glycerol was removed.

Synthesis of biodiesel stage 3: Post treatment process:

The transesterified product (methyl esters or raw biodiesel) was mixed gently with distilled water (30% volume of distilled water to volume of biodiesel) at 60± 5ºC in order to remove impurities like catalysts. The mixture was allowed to settle under gravity for 8 h. The settled layer of mixture with impurities was drained out. Water wash was repeated till the pH of drained water was measured in the range 6 to 7. After washing, the final product was again heated to 120ºC for 3 to 4 hours to remove water.

Formulations Antioxidant/Biodiesel:

Up to 1000 ppm of antioxidant was found to dissolve in the biodiesel samples. Each antioxidant was added to biodiesel B100 at the concentration of between 250 to 1000 mg/kg. The chemical structures of antioxidants are shown in Fig. 1. The different binary blends were prepared by mixing different solid phase antioxidants at weight ratios of 1:1. The different antioxidant blends combination as Table 1, with a total loading of up to 1000 ppm, were added to biodiesel B100 and mixed thoroughly until dissolved.



BHA BHT TBHQ Propyl gallate

Fig. 1: Chemical Structures of antioxidants tested

Table 1: Antioxidant combination add to B100

Sample number (Identification)	Concentration (mg/kg)	Basic Compostion
1	Control	No additive (anti-oxidant)
2,3,4	250,500,1000	TBHQ
5,6,7	250,500,1000	PG
8,9,10	250,500,1000	BHT
11,12,13	250,500,1000	BHA
14,15,16	250,500,1000	TBHQ:PG (1:1)
17,18,19	250,500,1000	TBHQ:BHA(1:1)
20,21,22	250,500,1000	TBHQ:BHT(1:1)

Analysis:

Initial water content of biodiesel with and without the addition of antioxidant was determined by Karl Fisher method using a Metrohm 831 KF Coulometer instrument (Herisau, Switzerland).

The stability of biodiesel was monitored by peroxide value determination (PV) and total acid number (TAN), where the samples were sampling at intervals of 2 weeks and analyzed. The total acid number levels of the prepared samples were determined according to the ASTM D664 (2011) method, and peroxide value levels according to the method used for peroxides in oils and fats AOAC (2000).

RESULTS AND DISCUSSION

Physical property data on the five types of biodiesel samples are given in Table 2. On the whole, the values were within the limits given by ASTM D6751 (2011).

Table 2: Initial Properties of Produced Biodiesel Samples

Properties	ASTM Method (2011)	ASTM specification	Measured value
Total Acid number (mg KOH/g)	D 664	0.5 max	0.20
Water content (% volume)	D6304 Coulometric KF	0.05 max	0.045

Effects of Different Concentration of anti-oxidant on the peroxide value (PV) of biodiesel:

Fig. 2 shows the PV of biodiesel B100 as a function of the concentration of added antioxidant. The antioxidants were added to the biodiesel B100 in a concentration range between 250 to 1000 ppm. Generally, the PV of samples was observed to decrease with the increasing antioxidant concentration. PG was found to be the most effective antioxidant in terms of stabilizing PV over week 8 at the range of concentration between 500 to 1000 ppm, followed by combination antioxidant of TBHQ-PG and TBHQ. However, with the addition of BHA, BHT, TBHQ: BHT and TBHQ:BHA antioxidant combination from 250-1000 ppm , it was found PV to increasing after 8 weeks, with BHT exhibiting the highest PV increase even at concentrations 1000 ppm.

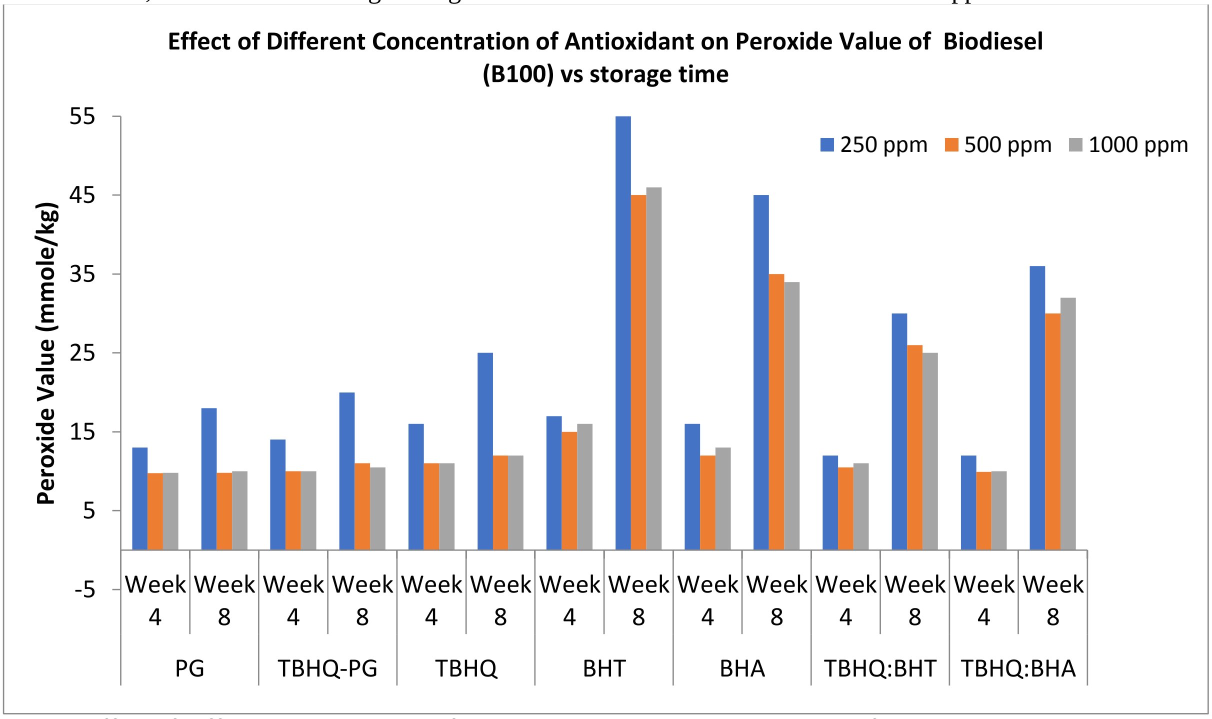


Fig. 2: Effect of different concentration of anti-oxidant on peroxide value level of stored biodiesel B100 vs. storage time

Effects of Different Concentration of antioxidant on the total acid number (TAN) of biodiesel:

Fig. 3 shows and summarizes the effect of different concentration of anti-oxidant on total acid number (TAN) of stored B100 vs. storage time. For biodiesel B100, the addition of antioxidant at concentration 250 ppm displayed noticeable increase in TAN. BHT gave the highest TAN increase at 250 ppm, followed by BHA, TBHQ-PG, and TBHQ-BHA (Fig. 3). It was noted that PG followed by binary TBHQ-BHT and TBHQ had almost the same effectiveness in stabilizing biodiesel at concentration 500 and 1000 ppm. For the effectiveness of antioxidants concentration on the of grease trap oil-based biodiesel at 500 ppm: PG produced the best improvement to stabilizing PV, TBHQ was the second most effective antioxidant followed by TBHQ- BHT. The effect of PG, TBHQ, BHA, and BHT are consistent with a previous study with frying oil based biodiesel (Mittelbac *et al*., 2003). TBHQ also could be used as good additive for recycled cooking oil methyl ester stability (Schober *et al*., 2004).

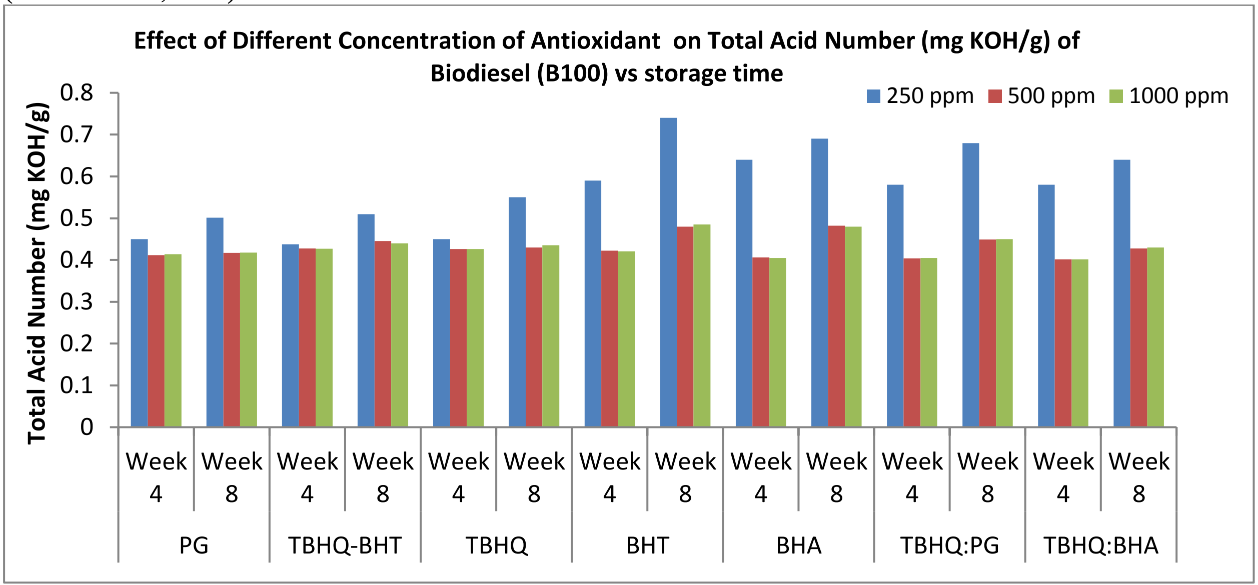


Fig. 3: Effect of different concentration of anti-oxidant on tptal acid number (TAN) of stored B100 vs. storage time.

Effect of different combination of antioxidants on peroxide value level of stored B100:

Fig. 4 shows and summarizes the peroxide value (PV) of biodiesel B100 with different antioxidants as a function of storage time. The effect of different antioxidants on biodiesel based is as follow: PG, TBHQ-PG combination and TBHQ gave the best result, followed by TBHQ-BHT combination, TBHQ-BHA, BHA and BHT. Monitoring of peroxide levels indicated the effect of antioxidants on oxidation that is to slow down the buildup of peroxide, which in turn stabilizes the oxidation of biodiesel.

The PV for untreated biodiesel B100 increased with time, and reached more than 80 mmoles/kg after 12 weeks. Samples with antioxidants PG, TBHQ-PG and TBHQ showed a very slow increase in PV during 12 weeks period, maintaining below 10 mmoles/kg to enable oxidation occurs. Other antioxidants such as BHA, BHT, combination of TBHQ-BHA and TBHQ-BHT gave a slight increase in PV level during the first 7 weeks period then significantly increased, up to 70 mmoles/kg after 12 weeks. This indicates that biodiesel B100 was still in good condition and not degraded up to 7 weeks.

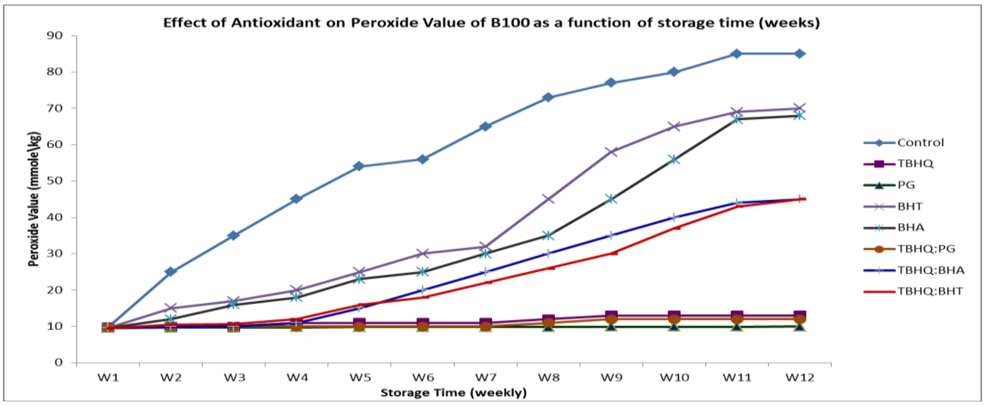


Fig. 4: Effect of different combination of anti-oxidant on peroxide value level of stored B100 as a function of storage time (weeks)

Effect of different antioxidants on total acid number:

Fig. 5 shows the total acid number (TAN) of biodiesel B100 with different antioxidants as a function of storage time. The acid number for untreated biodiesel B100 increased with time, and reached more than 0.5 mg KOH/g which exceeded ASTM D6751-11 specification after 3 weeks storage. Samples with antioxidants PG gave the best result follow by TBHQ, TBHQ-BHT, TBHQ-BHA and TBHQ-PG. All the treated B100 with these antioxidants combination has shown no significant increase of TAN and it values remained below 0.5 mg KOH/g during 12 weeks storage.

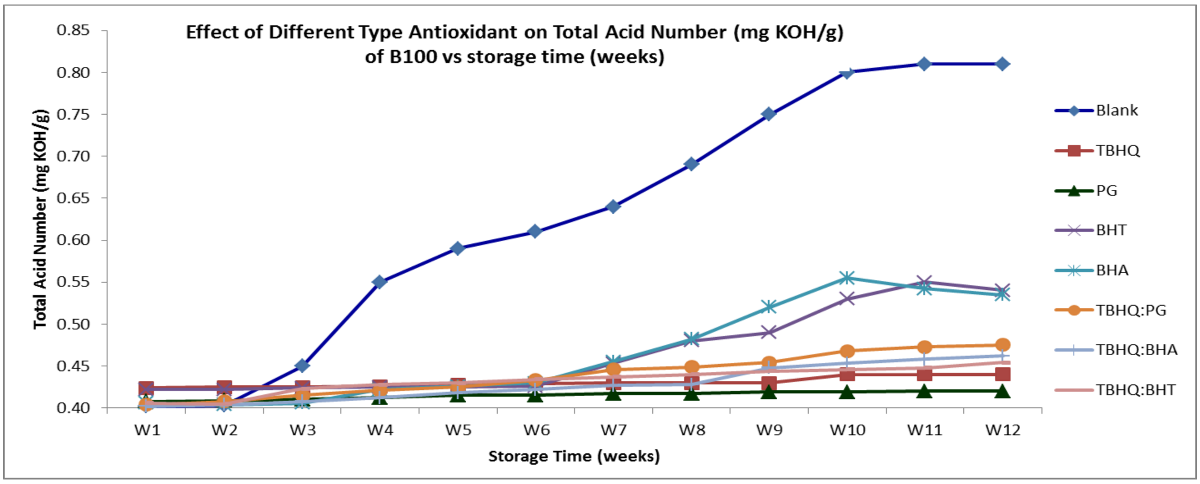


Fig. 5: Effect of different anti-oxidant on Total Acid Number (TAN) level of stored B100

Conclusion:

This study showed the effectiveness of synthetic antioxidants butylated hydroxyanisole (BHA), butyl-4-methylphenol (BHT), t-butyl hydroquinone (TBHQ) and propyl gallate (PG) in improving the oxidative stability of from grease trap oil based biodiesel (B100) at the varying concentrations between 250 and 1000 ppm. Some binary mixtures of antioxidants are more effective in improving oxidative stabilities of biodiesel B100 than individual ones, suggesting a synergistic interaction which may be important in the development of suitable blends. The best synergy to control PV and TAN was produced by the PG blend.

Results indicated that the storage stability of grease trap oil based biodiesel decreased with time. The addition of the antioxidant PG can improve and maintain oxidative and storage stability of the biodiesel B100 over a 12 weeks period. The binary combination TBHQ: PG and TBHQ: BHT also showed better performance than either individual antioxidant or can improve oxidative and storage stability of grease oil-based biodiesel (B100) for up to 12 weeks.

REFERENCES

Almeida, L.R., A.L. Silva, F.H.N. Souza, A.A. Hidalgo, M.L. Vega, H.N. Cunha and M.A.S. Rios, 2011. Evaluation of Antioxidant Potentiality of Compounds Derived from Biomass for Application in Biodiesel from Soybean Oil. Química no Brasil, In press.

AOAC 965.33, 2000, Official Methods of Analysis of AOAC Inc, Arlington VA, U.S.A 17th Edition.

ASTM D664-11ae1, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, ASTM International, West Conshohocken, PA, 2011, www.astm.org

ASTM D6751-15ce1, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2015, www.astm.org

Frankel, E.N., S.-W. Huang, J. Kanner and J.B. German, 1994. Interfacial phenomenain the evaluation of antioxidants: bulk oils vs. emulsions. J. Agric. Food Chem, 42: 1054-1059.

Tyson, K.S., 2006. Biodiesel Handling and Use Guidelines (3rd Ed.), US DOE/GO-102006-2358.

Mittelbac, M. and S. Schober, 2003. The influence of antioxidants on the oxidation stability of biodiesel. Journal of the American Oil Chemists Society, 80: 817-823.

Schober, S. and M. Mittellbach, 2004. The impact of antioxidants on biodiesel oxidation stability. European Journal of Lipid Science and Technology, 106: 382-389.

Sendzikiene, E., V. Makareviciene and P. Janulis, 2005. Oxidation stability of biodiesel fuel produced from fatty wastes. Polish Journal of Environmental Studies, 14: 335-339.

Venkanna, B.K. and R.C. Venkataramana, 2009. Biodiesel production and optimization from Calophyllum inophyllum linn oil (honne oil) – A three stage method. Bioresource Technology, 100: 5122-5125.