

ABSTRACT

This study investigates the impact of various synthetic phenolic antioxidants on the oxidation stability of biodiesel blends with the employment of the modified Rancimat method. The experimental results revealed that an improvement in oxidation stability could be achieved with all antioxidants tested. Propyl Gallate (PG) displayed the strongest effectiveness in neat biodiesel, whereas their use in biodiesel blends showed a greater stabilizing potential. During a naturally ageing process of the biodiesel blends which was conducted for a period of 06 weeks, samples were taken every week to measure the induction period, peroxide value, iodine value, acid value, calorific value and kinematic viscosity properties. This process was designed in such manner to simulate the ageing of an automotive biofuel stored in the fuel tank of a vehicle. The results showed a sharp decrease in fuel stability over time. Although limited effects were observed in viscosity, the acid value was significantly increased over time. The addition of antioxidants resulted in some increases in viscosity and acid value of the biodiesel blends

KEYWORDS: Biodiesel, oxidation, anti-oxidants, storage stability

I. INTRODUCTION

Bio-diesel is a renewable fuel, biodegradable and non-toxic. It is an ester based oxygenated fuel made from any vegetable oil (edible or non-edible) or animal fat. Bio-diesel is produced by a simple chemical reaction between vegetable oil and alcohol in the presence of an acid or base as catalyst. It contains around 10% built-in oxygen by weight and has no sulphur and has excellent lubricity properties. Built-in-oxygen makes it more efficient fuel than petro-diesel hence its cetane number is higher than that of petro-diesel. It can be blended with petro-diesel in any proportion. Bio-diesel is the name of the clean burning alternative fuel, produced from domestic, renewable resources. Bio-diesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a bio-diesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulphur and aromatics. It is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D6751 specifications for use in diesel engines. Bio-diesel refers to the pure fuel before blending with diesel fuel.

1.1 Statistical report

The National Bio-diesel Board (NBA) in the US reported that an estimated 5 million gallons of Biodiesel were sold in 1999, followed by 2 million gallons in 2000, 5 millions gallons in 2001, 15 million gallons in 2002 and an estimated 25 million gallons in 2003 respectively. It is estimated that during 2004-2005, an estimated 35 million gallons of bio-diesel is made in the US and it is likely to reach 70 million gallons in the US in 2006. Bio-diesel operates in conventional engines. Just like petroleum diesel, bio-diesel operates in compression-ignition engines. Essentially no engine modifications are required, and bio-diesel maintains the payload capacity and range of diesel.

1.2 Energy Scenario in India

India's incremental energy demand for the next decade is projected to be among the highest in the world. With increasing growth rate of GDP, total primary commercial energy consumption has increased from 350 million metric tones of oil equivalent (MMToE) during 2003-04 to 380 MMToE at present. Consumption of petroleum has increased from 3.5 million metric tones (MMT) in 1950-51 to 17.9 MMT in 1970 and 843 MMT

in 1997-98 and to more than 120 MMT at present. It is estimated that the demand for petroleum is 234 MMT in 2019-20. Domestic production of oil in 2004-05 is 33 MMT. Diesel consumption in 2004-05 for import of petroleum products and it is estimated to cost approximately Rs. 1, 75, 000 .00 crores in 2005 respectively.

There is increase in the growth rate of expenditure on import of petroleum to the tune of 46 percent from 2004-05 and 2005-06. More than 70 percent of India's total petroleum consumption is imported from international market, which itself has become more volatile than ever. International crude prices are soaring to new highs. Petroleum is predominately (46 percent) consumed in transport sector. The fuel-mix in transport sector shows that about 80 percent consumption in this sector is a High Speed Diesel (HSD). The projected demand for HSD in the country by 2005-07 is 52 MMT and on present indications, by 2011-12, it could increase to 67 MMT. Petroleum resources are finite and therefore search for alternative fuels is continuing all over the world. Bio-diesel is a renewable fuel and it can be made from any edible, non-edible vegetable oil including waste oil development of Bio-diesel as an alternative and renewable source of energy for transport sector has become important in the national effort towards self-reliance, an important component of the strategy for energy security.

1.3 Motivation of the present Investigation

From the above literatures, it is visualized that biodiesel is highly influenced by the presence of high unsaturated fatty acid that is the main culprit for oxidation, and very few researchers have used the anti-oxidants to reduce its impact. Although many papers exhibit the stability work on Jatropha, Mahua etc. but very less or no literatures has been stated on Karanja oil. Therefore, keeping in mind the above motivation we have thought of carrying out the experimentation to determine the stability (Oxidation and Storage) of karanja oil and compare its relevant data's with that of conventional diesel fuel.

1.4 Objective of the present Investigation

1. To prepare Karanja oil methyl ester.
2. To determine the effectiveness of different antioxidants blending with biodiesel having higher oxidation stability.
3. To measure the performance and emission characteristics of Karanja biodiesel blended with different antioxidants and its comparison with that of conventional diesel

II. MATERIALS AND METHODS

2.1 Transesterification Process

Transesterification is a process of producing a reaction in triglyceride and alcohol in presence of a catalyst to produce glycerol and ester. Molecular weight of a typical ester molecule is roughly one third that of typical oil molecule and therefore has a lower viscosity. Alkalis (NaOH, KOH), acid (H₂SO₄.HCL), or enzymes (lipase) catalyzed reaction. Alkali catalyzed Transesterification is faster than acid catalyzed Transesterification is most often used commercially, because the reaction is reversible, excess alcohol is used to shift the equilibrium to product side. Alcohols are primary and secondary monohydric aliphatic alcohols (1-8 C atoms). In the Transesterification process, methanol and ethanol are more common. Methanol is extensively used because of its low cost and its physiochemical advantages with triglycerides and alkalis are dissolved in it.

2.2 Determination of Physico Chemical Properties

2.2.1 Density

Thickness is defined as the ratio of mass to volume. The sub-atomic weight of biodiesel helps in increasing its value. The steadiness of biodiesel mixes diminish with hike in the amount of its constituents. The thickness of mixed biodiesel gets slightly changed. Thickness also additionally gets influenced by the temperature impact.

2.2.2 Viscosity

Viscosity should be given due importance for satisfactory engine output. It is characterized as the opposing force offered to the flow. More of its value makes hindrance at the time of supply as well as mixing with incoming air thereby differing burning. Previously it has been demonstrated by several experiments that the consistency diminishes as the working temperature rises up and increases when the biodiesel is preserved for a long period at a particular temperature. As the creation of peroxides arrives at a specific value viscosity begins to move up. The thickness of biodiesel is hardly influenced by antioxidants.

2.2.3 Flash point

The blaze point is characterized as the minimum temperature where fluid evaporates to make a combustible blend. It should be given utmost priority while evaluating the general combustibility risk of a material. Different variables have roll in the adjustment of this value. Biodiesels from different sources have different blaze values. This blaze value is affected by quantity of twofold bonds and carbon molecules.

2.2.4 Total Acid Number (TAN)

Amount of potassium hydroxide needed for neutralisation of unit mass of a substance is termed as total acid number. It is also named corrosive esteem or causticity value. TAN indicates the measure of acid in oil. Temperature, stockpiling time impact it. The TAN value enhances with rise in storing period, and due to this the oxidation steadiness diminishes. It relies upon the biodiesel composition which implies that the biodiesel contains of mono esters that have a tendency to experience the ill effects of less oxidative steadiness.

2.2.5 Total Base Number (TBN)

Ability of oil to absorb acids resulting from burning of fuel is called TBN. It may be portrayed as the estimation of basic added substances in oil with a specific end goal to keep away from oxidation and erosion. As indicated by the arrangement of acidic items with respect to the oxidation of the biodiesel fuel, the TBN indicates lubrication characteristics. TBN diminishes as the oxidation steadiness of biodiesel diminishes and enhances due to instability of oxidation.

2.2.6 Induction Period (IP)

The period of time before rapid oxidation is known as induction period. It is the estimation of opposition to oxidation and otherwise narrated as oxidative steadiness file. In light of a few investigations, it is seen that this time frame directly depends on the test temperature. To prevent degradation the biodiesel should be kept at cold space. Amid the storing period, the biodiesel get effectively oxidized and oxidised biodiesel ensures decreased IP.

2.2.7 Acid Value

Acid Value is a measure of the acidic substances in fuel. The rate of change of rate changes of acid value in low storage condition is lower as compared to the high temperature condition. Higher ratio of diesel gives stability to the sample. Diesel is more stable without oxidation process as compared to biodiesel because of oxygen content in biodiesel.

III. RESULTS AND DISCUSSION

Table 1: Fatty acid composition of Biodiesel prepared from Karanja oil methyl ester

Fatty Acid	Molecular formula	Percentage	Structure
Palmitic acid	C16H32O2	11.65	CH ₃ (CH ₂) ₁₄ COOH
Stearic acid	C18H36O2	7.5	CH ₃ (CH ₂) ₁₆ COOH
Oleic acid	C18H34O2	51.59	CH ₃ (CH ₂) ₁₄ (CH=CH)COOH
Linoleic acid	C18H32O2	16.64	CH ₃ (CH ₂) ₁₂ (CH=CH) ₂ COOH
Eicosanoic acid	C20H40O2	+1.35	CH ₃ (CH ₂) ₁₈ COOH
Dosocanoic acid	C22H44O2	4.45	CH ₃ (CH ₂) ₂₀ COOH
Tetracosanoic acid	C24H48O2	1.09	CH ₃ (CH ₂) ₂₂ COOH

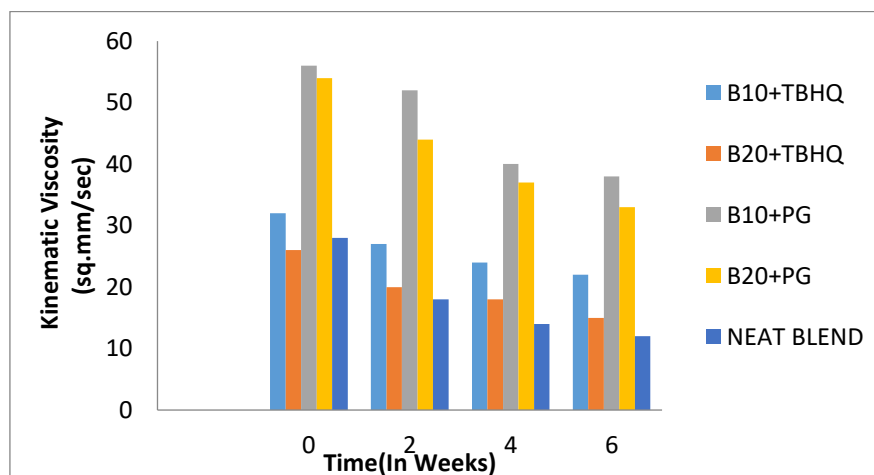
Table 2: Comparison of Properties Diesel and Karanja oil methyl ester with reference

Fuel properties	Units	Diesel	KOME
Density	Kg/m ³	830	876
Viscosity	mm ² /sec	3.12	4.96@ 25 °C
Fire Point	°C	65	112
Flash Point	°C	56	94
Cloud Point	°C	-8	-4.5
Pour Point	°C	-16	-10
Calorific Value	kJ/kg	43000	40200

Influence of ageing on quality parameters

Fig. 1 shows the viscosity changes for all biodiesel blends over the storage period of 06 weeks. As it can be seen, the addition of antioxidants led to slight increases in the viscosity of blends. Some increases in the viscosity were also observed for the samples tested at week 10, which can be considered as marginal. In general, viscosity starts to increase with the formation of peroxides when reach to a certain level and oxidized polymeric compounds that can lead to the formation of gums and sediments [15,24]. Under the present test conditions, there is no evidence of degradation products formation in the biodiesel blends, at least on a level that can affect the viscosity of the blend, which supports the hypothesis that the formation of these oxidation products requires a longer storage period of time, higher temperatures and direct expose to daylight and atmospheric oxygen.

Fig. 2 shows the changes in acid value over a storage period of 06 weeks. As expected, acid value increased with storage time for all biodiesel blends. This was particularly noticeable after week 6 where sharp increases in acid value were observed. This phenomenon may be attributed to the formation of peroxides and hydro peroxides, which may further oxidized into acids[15]. Acid values were also affected by the different antioxidants. In all cases, an important increase was found with the addition of antioxidants. The higher increases were observed with PG loading, an effect that was not unexpected due to the acid nature of these compounds.


Fig.1. Variation of Kinematic Viscosity with respect to Time duration (in weeks)

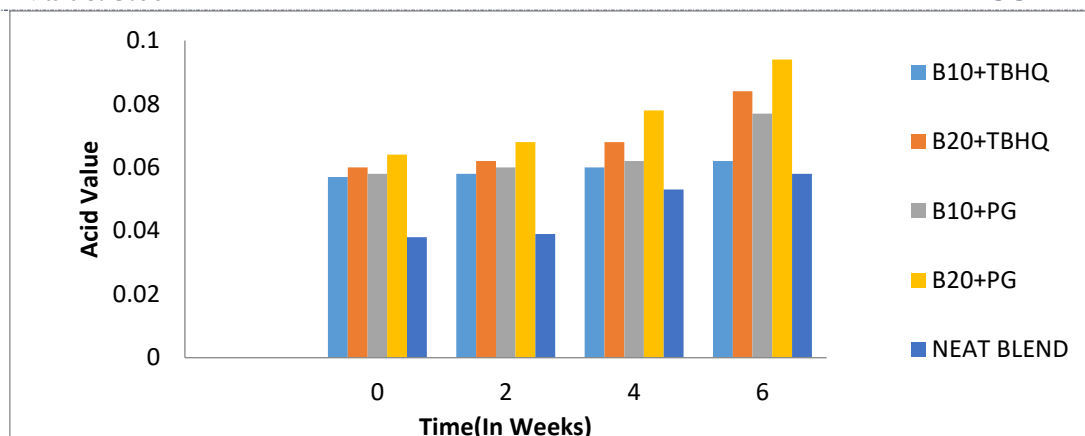


Fig. 2 Variation of Acid Value with respect to Time duration (in weeks)

Figs. 3, 4 & 5 shows the storage stability for the neat biodiesel blends and the B10, and B20 blends treated with the various antioxidant additives over a storage time of 06 weeks. The experimental results revealed that as the concentration of biodiesel increased, the oxidation stability of the final blends with diesel fuel decreased. The current results are in agreement with previous studies showing the same effect [20,21]. It is noteworthy that the neat biodiesel blends resulted in lower stability than those treated with antioxidants. Although the blends of B10 when first tested displayed an induction period above the minimum induction time of 20 h, the blend of B20 failed to meet the EN 590 limit. It should be stressed that all neat biodiesel blends remained well below the specification limit after the test at the second week, indicating a significant adverse effect of storage conditions, absence of antioxidants and fuel composition. As mentioned in previous paragraphs, all samples were stored in metallic containers and were fully exposed to daylight. Among the antioxidants tested, PG showed a greater effect on the stability of the finished blends. This was as expected, since both of these additives presented an increased stability performance with pure methyl ester. Although the use of TBHQ displayed an excellent performance in neat methyl ester, it was found a rather weak effectiveness when used in biodiesel blends. In a previous study conducted by Karavalakis and Stournas [22], it was reported that the addition of TBHQ showed an undesirable pro-oxidant interaction with the biodiesel blends, which in some cases the stability performance with TBHQ was found to be lower than the blends that were free of antioxidants. In terms of Rancimat hours, the effectiveness of most antioxidants for the B10 blends until week 8 and for the B20 blends until week 6. Beyond these points, the oxidation stability of most biodiesel blends was found below the specification limit of 20h.

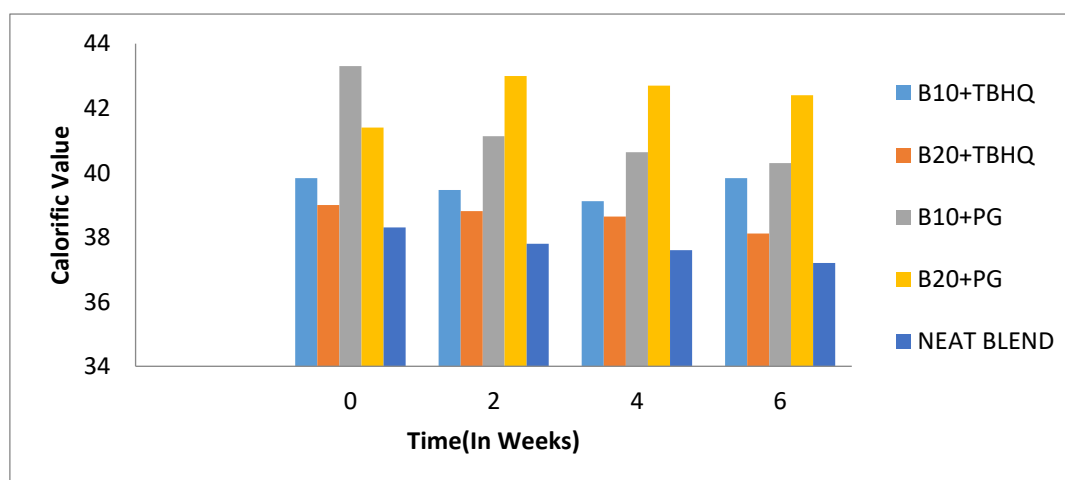


Fig. 3. Variation of Calorific Value with respect to Time duration (in weeks)

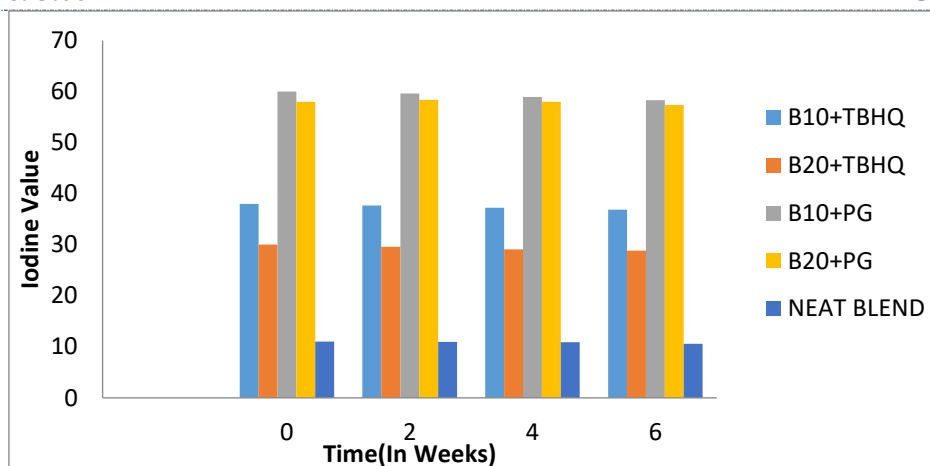


Fig. 4. Variation of Iodine Value with respect to Time duration (in weeks)

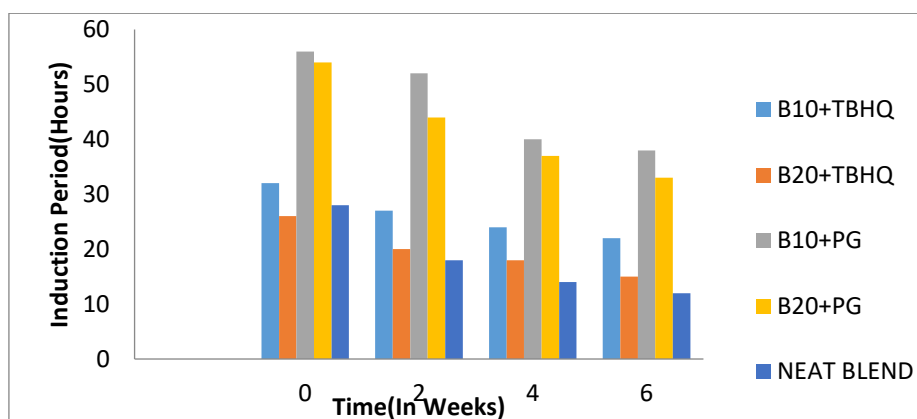


Fig. 5. Variation of Induction Period with respect to Time duration (in weeks)

IV. CONCLUSION

In this study, a commercially available biodiesel was treated with different phenolic antioxidants and blended with a typical automotive diesel fuel at proportions of 10 and 20% v/v, aiming to investigate the storage stability over 06 weeks. The experimental results revealed that PG were the most effective additives in neat methyl ester, whereas TBHQ was the least effective. Regarding the biodiesel blends it was found that with increasing biodiesel content, the stability of the finished blend decrease. The most effective antioxidants for the blends were found to be PG. Despite the fact that TBHQ offered an effective performance by significantly increasing the oxidation stability of neat biodiesel, a rather poor activity was observed when loaded in biodiesel blends. The naturally ageing process of biodiesel blends showed that oxidation stability can be adversely affected by storage conditions and time, leading to induction times below the minimum specification limit of 20 h after 2-3 weeks. The addition of antioxidants led to important differences in acid value and to limited effects in kinematic viscosity of the fuel blends. For all biodiesel blends, the acid value and to a lesser extent viscosity, tended to increase over storage time probably due to the formation of oxidation products such as peroxides and acids.

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