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Experimental Investigation On Stability And Ageing Impact Of Callophyllum Inophyllum Oil Methyl Ester With Diesel Blends

B.Prashanth[1],*, Shubham Pandey[1], Shubam Tiwari[1], Vishal kumar Gaurav[1], Vikash Kumar Parmar[1]

School of Mechanical engineering, Kalinga Institute of Industrial Technology (Deemed to be University), Bhubaneswar, Odisha-751024

Abstract: **Oxidation stability is one of the most significant parameters of fatty acid alkyl esters (Biodiesel) which primarily affects the biodiesel stability during prolonged storage. The product yielded from oxidation process may impoverish the fuel properties and finally affects the engine performance. The prolonged storage of biodiesel leads to oxidation instability which can be overcome by the utilization of synthetic antioxidants. The Calophyllum Inophyllum oil can be used as a source of biodiesel esterification and can be used as an alternative to present conventional fuels. The synthetic antioxidants are used to improve the stability of biodiesel during prolonged storage. Biodiesel has the capability in replacing the present conventional fuels, so stability plays an important role in commercialization of biodiesel. Biodiesel is otherwise called as green diesel as it is eco-friendly and which helps in maintaining the balance of the ecosystem. The present paper gives an experimental study of the usage of TAN & TBN in maintaining the stability of biodiesel.**

Key words: **biodiesel; esterification; Antioxidant; Blending**

1. Introduction

Biodiesel is a long chain alkyl ester prepared from edible or non- edible oils. As a developing country we depend mostly on non-edible fuels like karanja, jatropha, Calophyllum Inophyllum, Mahua, Madhuka Indika etc... for the preparation of biodiesel. The increase in demand for vehicles and the industries which uses conventional fuels for the generation of power has led to the excess utilization of conventional fuels which resulted in the emission of pollutant gases. The excess use of fossil fuels has led to the depletion and scientists are in their way to find an alternative and biodiesel is one amongst them. Biodiesel is prepared by esterification followed by transesterification. Biodiesel production involves 4 stages after which the biodiesel is tested for its performance characteristics and is compared with ASTM or European standards. In this paper callophyllum Inophuyllum is used as an alternative to the present solution[1]. Callophyllum Inophyllum is a slow growing and low branching tree and has its seeds all-round the year making the production of biodiesel easier and cheaper. The callophyllum Inophyllum yields thick green tamanu oil for medical use and hair grease. This indicates that the oil has more viscosity and the acid content is in between 20-40% and is indicated in table 1. The Callophyllum Inophyllum seed consists of 70-75% of non-edible oil which is thick and green in colour. The fatty acid methyl esters derived from callophyllum Inophyllum seed oil meets the major biodiesel requirements in United states (ASTM D 6751) and European standards (EN 14214). The average oil yield per hectare is 4680 kg oil/ hectare or 11.7 kg oil/tree.

Table 1. Physical Characteristics

Physical Character	Range
Iodine value	79-98
Acid value	20-40
Unsaponifiable matter	1.5% , maximum
Moisture	0.5%, Maximum
Refractive Index 30^{0}C	1.460-1.470
Saponification value	190-205

Fig 1. Calophyllum Inophyllum seeds

2. Effect of Free fatty acid on stability of biodiesel:

Free fatty acids are formed due to the hydrolysis of fats and oils and are less stable than neutral oil. They readily oxide and reduce the stability of biodiesel which results in the change of physical and chemical properties. The more the presence of fatty acids the more is the percentage of acid in the oil[2]. So the percentage of acid can be estimated by titrating the oil with base (KOH or NaOH). For the present oil the percentage of acid was found to be 34% and is neutralized using KOH and methanol. The free fatty acids present in callophyllum Inophyllum is shown in table 2.

Table 2. Percentage of Fatty Acids in Callophyllum Inophyllum oil

Fatty Acid	Percentage
Palmitic Acid	14.8-18.5
Stearic acid	6.0-9.0
Oleic acid	36-5
Linolenic acid	16-29
Erucic acid	2.5-3.5

3. Production of Biodiesel

In order to neutralize the oil and to reduce the viscosity transesterification is done in which the oil having long chains of triglycerides are converted into small chains of methyl esters[3]. The production of biodiesel involves 4 stages namely.

- Pre-treatment of oil
- Acid catalysed transesterification process
- Base catalysed transesterification process
- Water wash

3.1. Pre-heating or pre-treatment of oil:

In this stage the oil is heated above 100^{0}C in order to remove water particles and some impurities are filtered by homogenous mixing using magnetic stirrer. Pre- heating also reduces the viscosity of the oil and increases the flow ability of oil.

Fig 2. Pre-heating of oil

3.2. Acid catalysed esterification process:

In this process the filtered oil is allowed to cool down up to 40^{0}C-45^{0}C. Esterification is a process of converting carboxylic acid into ester in the presence of a catalyst H_2SO_4 and Methanol[4]. The mixing of oil along with Methanol or Ethanol is done in the presence of acid and is heated up to 50^{0}C-55^{0}C.The mixture is heated continuously up to 3 hours and the temperature should be maintained below 55^{0}C as the evaporation temperature of Methanol is 55^{0}C. The products formed after esterification is murky solution and glycerol (90% Glycerine and 10% Impurities). The solution is allowed to settle down for 8-12 hours[5].

Fig 3. Acid Treatment

3.3 Base catalysed transesterification process:

The main stage of Biodiesel production is transesterification process in which the ester produced in esterification process is reacted with alcohol and Base in order to form another ester (Biodiesel). The solution is heated for 3 hours and allowed for settling. The by-product formed during the transesterification is glycerol[6].

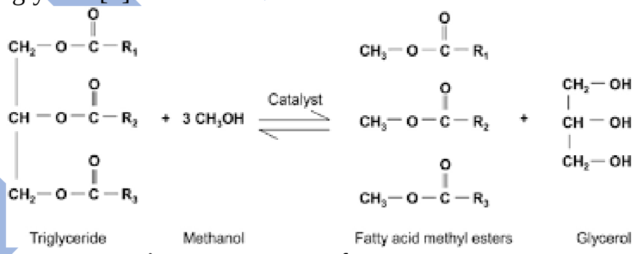

Fig:-4. Trans-esterification process

Fig 5. Settling of Biodiesel and Glycerine

3.3 Water wash:

The final stage of biodiesel preparation is water wash in which distilled water is added in the ratio of 1:1. Distilled water is used as it is free from minerals. The oil and distilled water is added and is bubbled using bubbler. 4-5 drops of Ortho phosphoric acid is added to the solution and is bubbled up to 1 hour[7]. The water wash is done until pure water is visible along with oil.

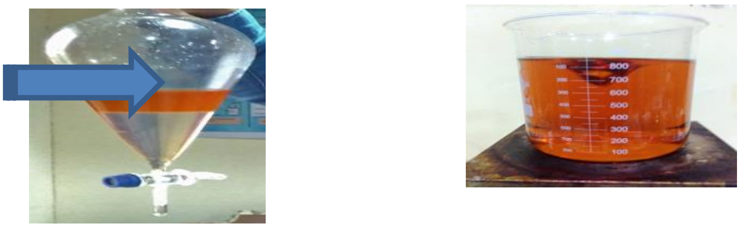

Fig 6. Water wash

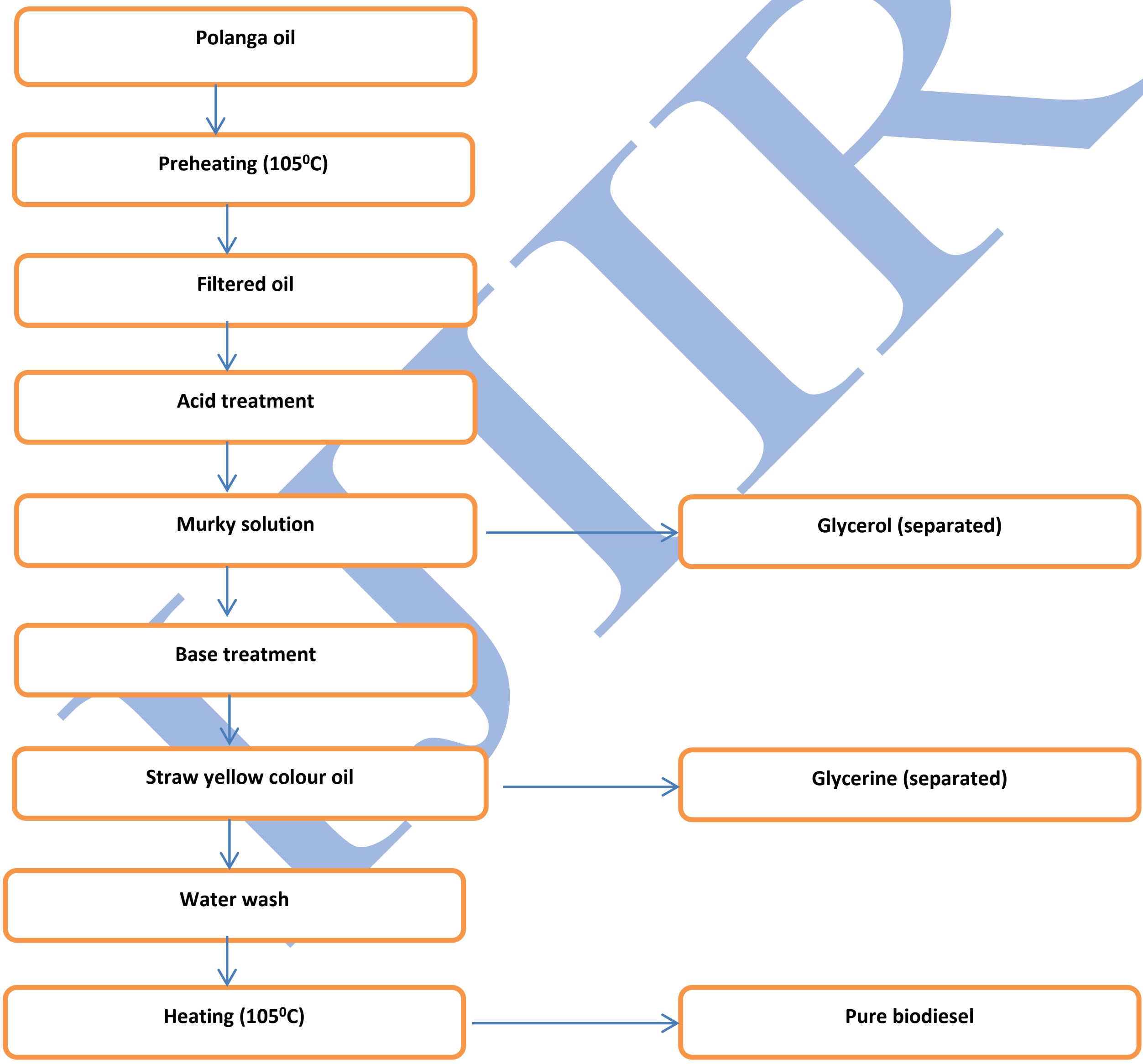

Fig 7.Flowchart of biodiesel production

4. Result & discussion

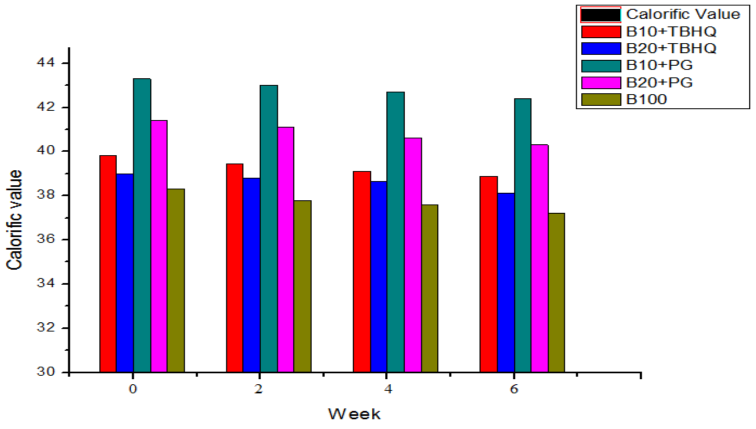

Fig 8. Calorific values vs time (in weeks)

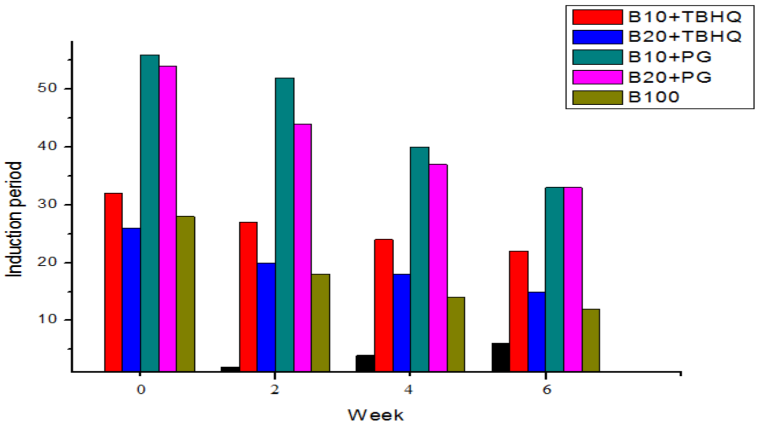

Fig 9. Induction period vs Time (in weeks)

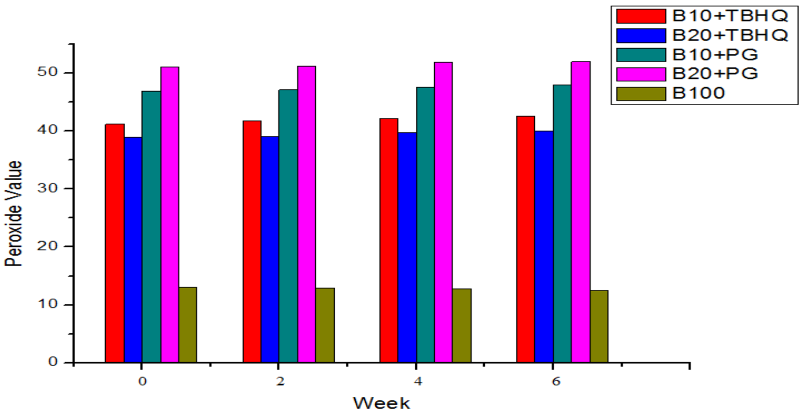

Fig 10. Peroxide value vs Time (in weeks)

Figs. 8, 9 and 10 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 [8].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 [9],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 20 h.

6.2. Influence of ageing on quality parameters

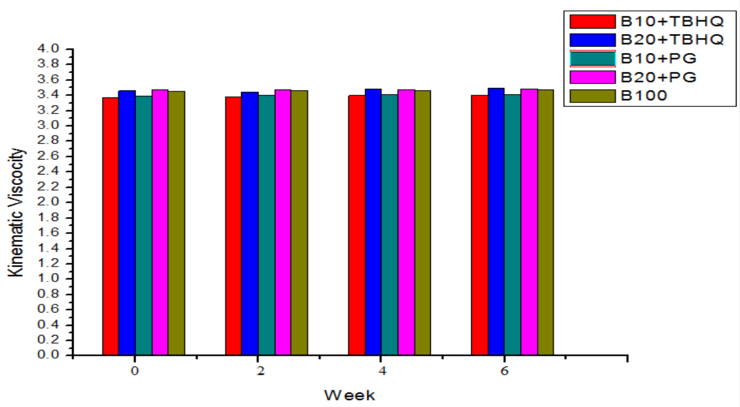

Fig 11. Kinematic viscosity vs Time (in weeks)

Fig. 11 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 [10]. 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.

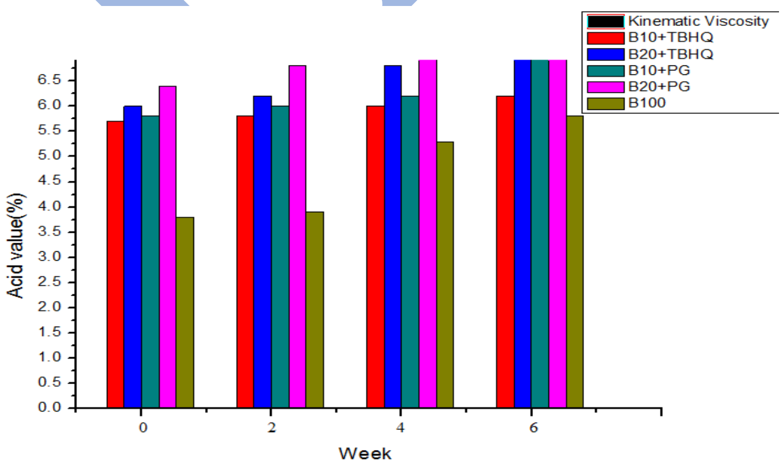

Fig 12. Acid Value (%) vs time (in weeks)

Fig. 12 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[11-12]. Acid values were also affected by the different antioxidants.

5. 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 a 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.

6. References

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