

INVESTIGATION OF ANTIOXIDANTS IN MITIGATING AGEING IN KARANJA BIODIESEL

Garcia, L., Martinez, R., Lopez, A., Ramirez, C.

School of Civil Engineering, National Polytechnic Institute, Mexico City, Mexico

ABSTRACT

This Biodiesel may be portrayed as a substitute or supplement for diesel. But its thickness, consistency, streak point, corrosive number (TAN), and base number (TBN) must be analysed thoroughly by using internationally accepted instrument.. Also, oxidation steadiness of the specimens is measured by the enlistment period utilizing proper instrument for different samples of biodiesels. Almost all specimens met the American standard detail in regards to the enlistment time frame, with the exception of Jatropha and its biodiesel. most exceedingly terrible outcome for TBN esteem obtained from PME and COME.

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

I. INTRODUCTION

As a substitute to traditional fuel biodiesel is very promising. It is prepared by adopting basic compounding processes on raw vegetable oils or animal fat oils. It can be used to run diesel motor or vehicle without making any adjustment. It is justifiably called as green fuel in view of the factors like sustainability and eco friendliness like reduction in liberation of exhaust gasses. Biodiesel is much suitable for fundamental elements like soil, air and water. In its pure form it is user friendly and can be degraded easily, which is utmost essential in critical situations. It is further credited with less harmful emissions as either it is totally free from sulphur or contains negligible amount of sulphur in its composition. After being blended to diesel in suitable proportions it ensures better and rapid combustion. Biodiesel is prepared by transesterification process that includes response between triglycerides in presence of methanol or ethanol. Owing to less price and rapid reaction methanol is a favourable choice. Alkyl ester and glycerol are the main by products of such response.

1.1 National Statistic for Bio-diesel

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 current 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.

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 Kinematic 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 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.

2.2.5 Acid Value

Acid Value is a measure of the acidic substances in fuel. The rate of change of rate changes of aid 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 in biodiesel.

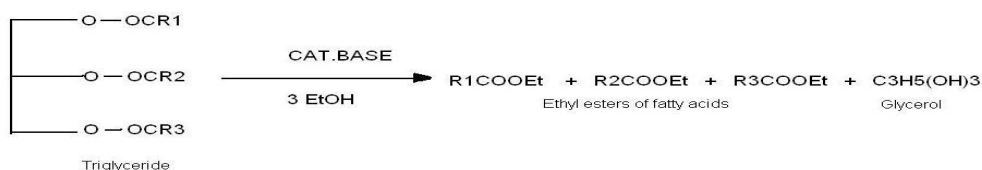


Fig.1 Reaction scheme for Transesterification

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

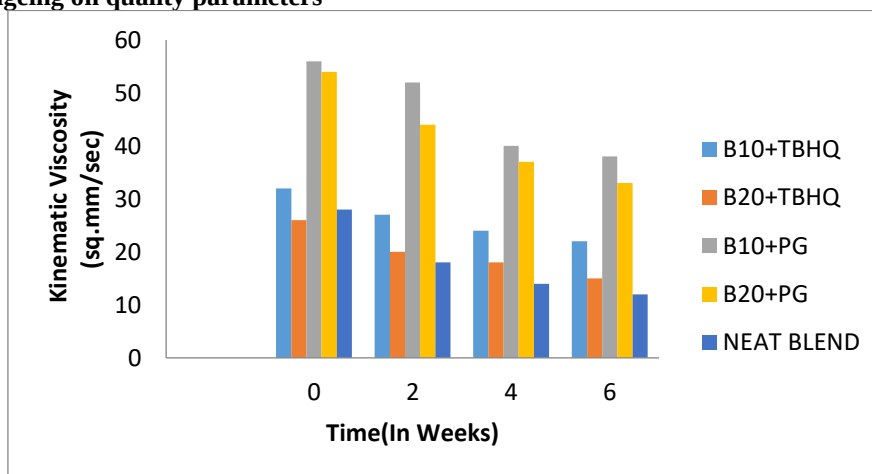


Fig.2. Variation of Kinematic Viscosity with respect to Time duration (in weeks)

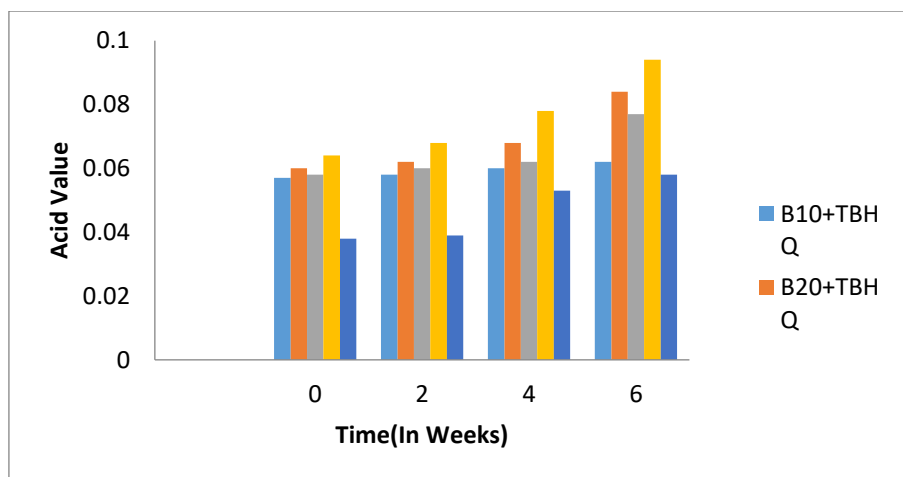


Fig. 3. Variation of Acid Value with respect to Time duration (in weeks)

Fig. 2 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. 3 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.

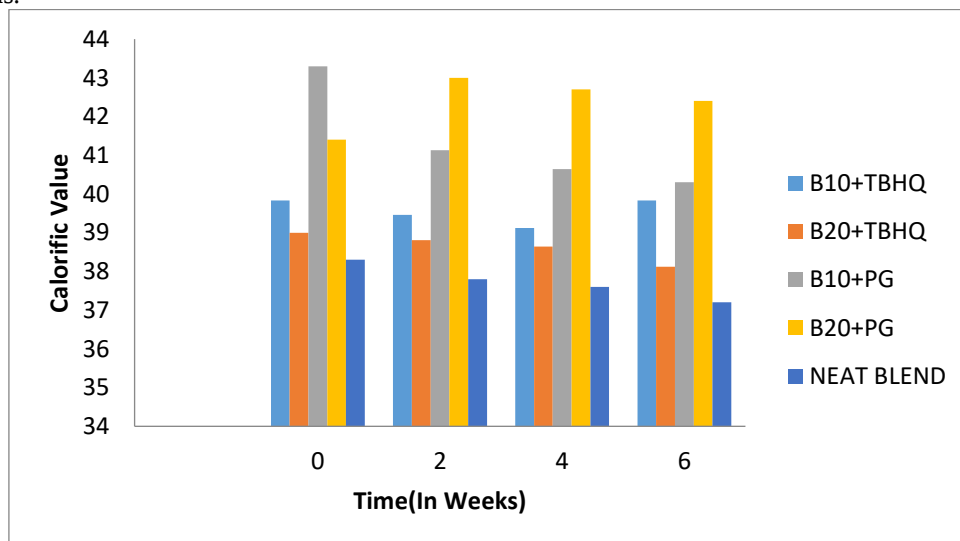


Fig. 4. Variation of Calorific Value with respect to Time duration (in weeks)

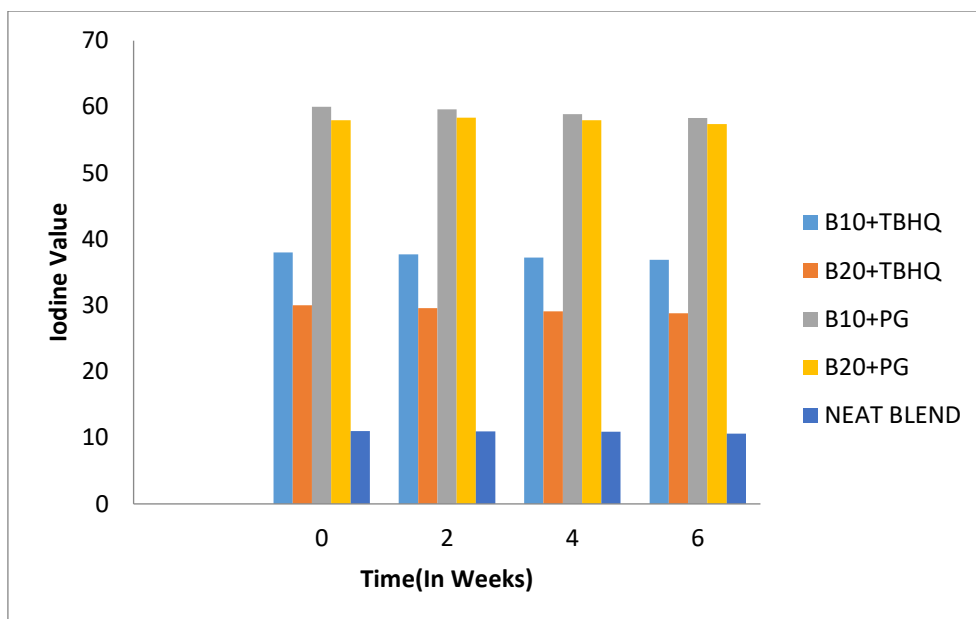


Fig. 5. Variation of Iodine Value with respect to Time duration (in weeks)

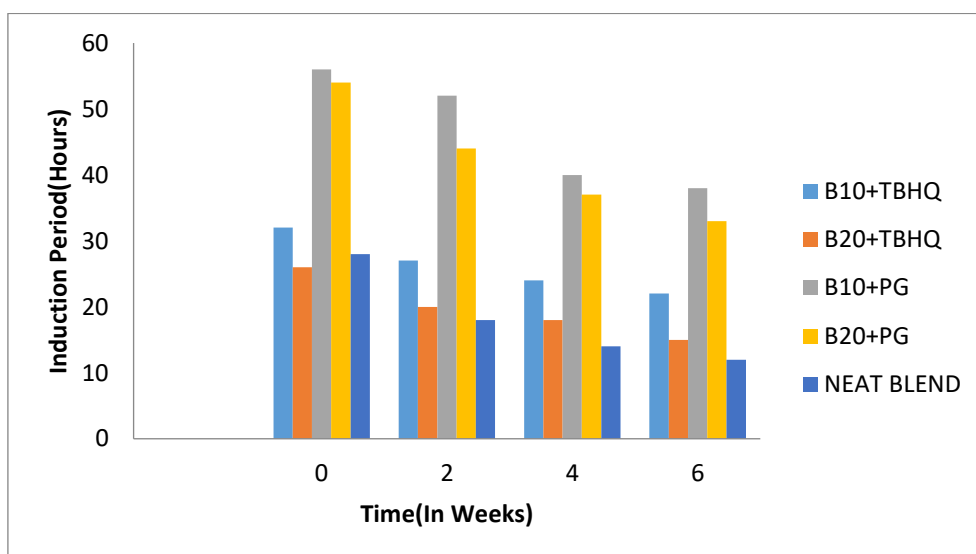


Fig. 6. Variation of Induction Period with respect to Time duration (in weeks)

Figs. 4, 5 & 6 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.

IV. CONCLUSION

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. 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.

V. ACKNOWLEDGEMENTS

The authors are very much grateful and thankful to the School of Mechanical Engineering, KIIT University, for providing the experimental setup and space for carrying out the experimentation.

VI. REFERENCES

- [1] KS. Chen, YC. Lin, LT. Hsieh, LF. Lin, CC. Wu. Saving energy and reducing pollution by use of emulsified palm-biodiesel blends with bio-solution additive. *Energy*, 2010,36, pp.2043-8.
- [2] Dunn RO. Antioxidants for improving storage stability of biodiesel. *Biofuels, Bioproducts and Biorefining* 2008;2:304-18.
- [3] Nayak SK, Mishra PC. Application of Nagchampa biodiesel and rice husk gas as fuel. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. 2016;38:2024-30.
- [4] Sarin A, Arora R, Singh NP, Sarin R, Malhotra RK, Sharma M, et al. Synergistic effect of metal deactivator and antioxidant on oxidation stability of metal contaminated Jatropha biodiesel. *Energy* 2010;35:2333-7.
- [5] Nayak SK, Mishra PC. Emission from a dual fuel operated diesel engine fuelled with Calophyllum Inophyllum biodiesel and producer gas. *International Journal of Automotive and Mechanical Engineering*. 2017;14:3954-69.
- [6] Knothe G. Some aspects of biodiesel oxidative stability. *Fuel Processing Technology* 2007;88:669-77.
- [7] McCormick RL, Ratcliff M, Moens L, Lawrence L. Several factors affecting the stability of biodiesel in standard accelerated tests. *Fuel Processing Technology* 2007;88:651-7.
- [8] Nayak, CK., Pattanaik, BP., Nayak, SK. (2014). Effect of Preheated Jatropha oil and Jatropha oil Methyl Ester With Producer Gas on Diesel Engine Performance. *International Journal of Automotive and Mechanical Engineering*. 09, 1701-1722.
- [9] Paligova J, Jorikova L, Cvengros J. Study of FAME stability. *Energy and Fuels* 2008;22:1991-6.
- [10] Schober S, Mittelbach M. The impact of antioxidants on biodiesel oxidation stability. *European Journal of Lipid Science and Technology* 2004;106:382-9.
- [11] Nayak, SK., Mishra, PC. (2017). Analysis of a diesel engine fuelled with jojoba blend and coir pith producer gas. *International Journal of Automotive and Mechanical Engineering*. 14, 4675-4689.
- [12] Dunn O. Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). *Fuel Processing Technology* 2005;86:1071-85.
- [13] Tang H, De Guzman RC, Salley SO, Simon Ng KY. The oxidative stability of biodiesel: effects of FAME composition and antioxidant. *Lipid Technology* 2008;20:249-52.
- [14] Du Plessis LM, de Villiers JBM, Van der Walt WH. Stability studies on methyl and ethyl fatty acid esters of sunflowerseed oil. *Journal of the American Oil Chemists' Society* 1985;62:748-52.
- [15] Bouaid A, Martinez M, Aracil J. Long storage stability of biodiesel from vegetable and used frying oils. *Fuel* 2007;86:2596-602.
- [16] Bondioli P, Gasparoli A, Della Bella, Tagliabue S. Evaluation of biodiesel storage stability using reference methods. *European Journal of Lipid Science and Technology* 2002;104:777-84.
- [17] DeGuzman R, Tang H, Salley S, Simon Ng KY. Synergistic effect of antioxidants on the oxidative stability of soybean oil and poultry fat-based biodiesel. *Journal of the American Oil Chemists' Society* 2009;86:459-67.
- [18] Liang YC, May CY, Foon CS, Ngan MA, Hock CC, Basiron Y. The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. *Fuel* 2006;85:867-70.

- [19] Berrios M, Gutierrez MC, Martin MA, Martin A. Obtaining biodiesel from spanish used frying oil: issues in meeting the EN 14214 biodiesel standard. *Biomass and Bioenergy* 2010;34:312-8.
- [20] Karavalakis G, Karonis D, Stournas S. Evaluation of the oxidation stability of diesel/biodiesel blends using the modified Rancimat method. *SAE International Journal of Fuels and Lubricants* 2009;2:839-49.
- [21] Karavalakis G, Stournas S, Karonis D. Evaluation of the oxidation stability of diesel/biodiesel blends. *Fuel* 2010;89:2483-9.
- [22] Karavalakis G, Stournas S. Impact of antioxidant additives on the oxidation stability of diesel/biodiesel blends. *Energy and Fuels* 2010;24:3682-6.
- [23] Nayak, SK., Pattanaik, BP. (2014). Experimental Investigation on Performance and Emission Characteristics of a Diesel Engine Fuelled with Mahua Biodiesel Using Additive. *Energy procedia*. 54, pp. 569-579.
- [24] Das LM, Bora DK, Pradhan S, Naik MK, Naik SN. Long-term storage stability of biodiesel produced from Karanja oil. *Fuel* 2009;88:2315-8.