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Thermal Stability and Emission Analysis of Antioxidant Stabilized pure Coconut Oil Biodiesel

Ranjith B P[1], Krishnakumar K[2]

Head of Section, Mechanical Engineering, Government Polytechnic College Chelakkara, Thrissur, India[1]

Head of the Department, Mechanical Engineering , College of Engineering Trivandrum, Trivandrum, India[2]

Abstract: Biodiesel is defined as the mono-alkyl ester of vegetable oils and animal fats. Bio-energy is renewable and environment-friendly which is a clean-burning alternative fuel produced from vegetable oils. An investigation on the use of biodiesel prepared from coconut oil as fuel in a CI engine was carried out which included a study of the fuel properties. It was observed that the fuel properties viz. specific gravity and viscosity were unsuitable for use of straight vegetable oils whereas their methyl esters exhibited comparable viscosities with diesel fuel. All proportions of coconut oil methyl ester exhibited a considerable reduction in emission in CI engines when compared to diesel at all loads except at no load which confirmed the pollution reduction ability of coconut oil biodiesel. The specific fuel consumption of biodiesel is higher than diesel at all loads. The study indicated that coconut oil biodiesel is like diesel for CI engines, except for its high specific fuel consumption. But the biodiesel stability is affected by slow oxidation in the presence of light and atmospheric oxygen. The storage of biodiesel over a long period leads to degradation of fuel properly. Freshly prepared biodiesel shows reduced CO and NOx emissions than diesel. Long-term storage causes an increase in viscosity and density and a decrease in the heat of combustion. This study was conducted with Propyl Gallate as a synthetic antioxidant as the additive. Thermo-gravimetric analysis was carried out to check the thermal stability. The performance and emission studies were also carried out.

Keywords: Biodiesel, Antioxidant, TGA, Emission, KANE 900+, Alternative Fuel

I. INTRODUCTION

The scarcity of conventional fuels and environmental concerns leads to the query of alternative renewable sources of energy as a substitute for traditional fossil fuels to attain the incessant energy demand. Due to Shortage of petroleum resources and variation price of petroleum, we may not be able to depend on these sources in future. The alternatives should be technically feasible, economically competitive, environmentally acceptable with less harmful emission, and must be readily available [1]. Vegetable oils satisfy most of these requisites. The direct use of vegetable oils as fuels is restricted due to its high viscosity, low volatility, and the reactivity of unsaturated hydrocarbon chains. The conversion of vegetable oils to fatty acid alkyl esters (biodiesel) is the effective way to reduce the above problems encountered with vegetable oils. Vegetable oils are essentially mixtures of triglycerides of fatty acids like oleic, palmitic, stearic, linoleic and linolenic acids. In the trans-esterification process to prepare biodiesels, alcohols (methyl or ethyl) react with the triglycerides in vegetable oils in presence of a catalyst to form glycerol and simple esters. An excess alcohol is required to force the reaction to completion. The chemical reaction is as shown in Fig. 1.Various alkali metal compounds supported on various solids.

Biodiesel is biodegradable and non-toxic and thus preferred over fossil fuels. The properties such as higher cetane number, the absence of aromatics, high flash point, non-volatile nature, high lubricity etc. when compared with diesel and presence of 7-10 % oxygen by weight that can take part in combustion are the attractions of biodiesel. Since there is inherent oxygen content in the fuel, it will reduce the emission of Carbon monoxide (CO). It can be produced domestically, reducing our country's dependence on imported oil, thus making huge saving on imports. Biodiesel can be directly used in engines, without any modification or changes in fuel handling and delivery system. It makes a positive impact on agriculture and it can decrease global warming, which is the most pressing environmental challenge of 21st century.

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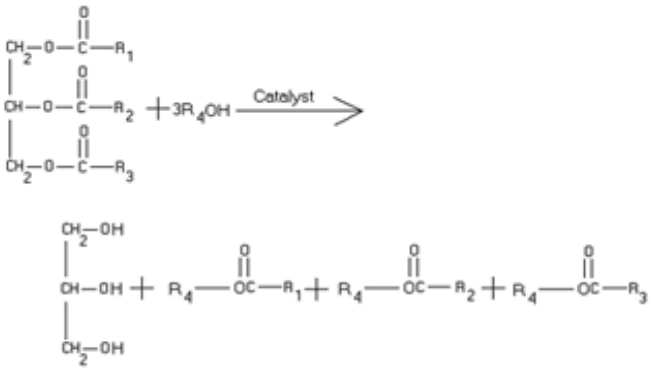

Fig. 1 Chemical Reaction. R1, R 2 and R3 represent the hydrocarbon chains of acids.
R4 is the alkyl group of the alcohol.

Thus biodiesel, the non-petroleum-based fuel consists of fatty acid alkyl esters derived by the transesterification of triglycerides. The purpose of the transesterification process is to reduce the viscosity of the oil. The reaction can be catalyzed by either homogeneous or heterogeneous catalyst. Homogeneous catalysts are acid, alkali or enzyme. The problems associated with homogeneous catalysts are in the separation of catalysts from the product, large amount of waste of water and the non-reusability of the catalyst. Compared with homogeneous catalysts, heterogeneous catalysts can provide green and recyclable catalytic systems [2]. Heterogeneous catalysts have a longer catalytic life. They are non-corrosive and easily separable from product phase. Heterogeneous catalysts used for biodiesel production are mainly solid base. The studies on the engine performance of biodiesel prepared via heterogeneous catalysis are rare. Present investigation targets on the engine performance, Thermo-Gravimetric Analysis(TGA) and hydrocarbon emission of the biodiesel prepared by the trans-esterification of coconut oil using a homogeneous catalyst and it is stabilised by synthetic antioxidant Pyrogallate. Our earlier paper [20], in which biodiesel has prepared from used oil by using a heterogeneous catalyst.

A. Experimental Materials

Biodiesel production by the trans-esterification of coconut oil over the homogeneous catalyst. 6000gm of oil (FAA <1) is poured into an inner vessel of biodiesel mini plant. 0.5 weight percentage NaOH (w.r.t oil) is weighed and added into 1:9 molars (w.r.t oil) methanol is taken in a beaker and mixed thoroughly with the help of a magnetic stirrer. This alcohol (Sodium Methoxide) solution is added to the oil. The inner vessel is equipped with a water condenser and kept in an oil bath at 65 degrees Celsius, maintained by a temperature controller and stirred for 1 hour. After completion of the reaction, the mixture is then taken out and then poured into a separating funnel and allowed to settle for 24 hours. Once the trans-esterification reaction is completed, two major products exist esters (biodiesel) and glycerol. The glycerol phase is much denser than the biodiesel phase and settles at the bottom of the reaction vessel, allowing it to be separated from the biodiesel phase. Phase separation can be observed.within 10 min. Since both glycerol and alcohol are highly soluble in water, water washing is very effective for removing both these contaminants in the biodiesel layer. Warm water prevents the precipitation of saturated fatty acid esters and retards the formation of an emulsion with the use of a gentle washing action. The top biodiesel layer was washed withdeionized water thrice. Then the biodiesel and glycerol phases are separated. Then water is removed from the biodiesel by the addition of anhydrous sodium Sulphate and filtered to remove the sodium Sulphate or by heating at a temp of 110 degrees for one hour. Methanol, anhydrous sodium Sulphate and phosphoric acid were purchased from Nice Chemicals, India. Solvents (Nice chemicals, India) used in this experiment were of analytical reagent grade.

Stability is one of the important criteria concerning fuel properties. The stability of biodiesel is lower than common diesel fuel. Biodiesel is susceptible to the oxidation due to its unsaturated fatty acid esters. The oxidative stability of biodiesel is affected by numerous factors. Ultraviolet irradiation, metal contamination, humidity, pigments, some enzymes and heating can affect biodiesel, deteriorating its fuel performance when exposed to oxygen. Oxidation is one of the significant stability concerns associated with biodiesel because it has a lower resistance capacity to oxidation and can easily be affected by air oxidation and cause the formation of deposits and gum, and the darkening of fuels as a result of the formation of contaminants, such as alcohols, acids, aldehydes, peroxides, etc. occur during long-term storage of biodiesel fuel. Both oxygen content and exposition time play an important role in the formation of undesired compounds, which can corrode the engines or clog the filters and injection systems of the engines. The biodiesel was then directly used in the engine for the performance test. Then separated the quantity into two samples and added a

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1000 ppm Pyrogallate antioxidant in one sample to provide stability to biodiesel. These samples were tested in two particular periods of the time interval of 6 months and one year.

B. Engine Test Procedure

Before starting the engine, maximum load of the engine was calculated. Start the engine at no load condition. Fuel supply is switched on and the decompression lever is engaged. The engine was started by manual cranking or by turn the ignition switch. The time taken for 10cc of fuel consumption is noted at no load. Cooling water is supplied for avoiding overheating.

Table I Engine Specifications

Sl. No	Parameters	Specifications
1	Bore	85 mm
2	Stroke	110 mm
3	Swept Volume	553 cm3
4	Clearance Volume	36.87 cm3
5	Rated Output	3.7kW @1500 rpm
6	Rated Speed	1500 rpm
7	Orifice Diameter	15 mm
8	Coefficient of Discharge	0.62
9	Loading system	Rope Drum dynamometer (Water cooled)

KANE 900 plus was the instrument used to check the emission of CO and NOx. The thermal conductivity of each gas has the ability to conduct heat at a specific rate. This property is utilized in the thermal conductivity detector. Heated metal filaments are exposed to the zero and sample gases. The amount of heat carried away by the gases changes the rate of cooling of the wire filament and, therefore its temperature. This temperature change causes a resistance change. Since the filaments are arranged in a Wheatstone bridge, the resistance change can be converted to an electrical current that is available as an output signal. By gradual loading, time for fuel consumption and manometer reading and emission content were noted.

C. Thermo-Gravimetric Analysis (TGA)

1) Procedure:

Thermal stability of fuel depends on activation energy(E) and frequency factor (A). In this work, the thermal stability of pure biodiesel and antioxidant stabilized biodiesels are compared. In the first sample of B100, 12 mg of bio-diesel were taken in the sample holder, which was surrounded by a furnace with temperature programming facility, in which heating rate was adjusted 10°C/min from 33.85°C to 450°C. And corresponding %mass loss was recorded. And in the second sample 17mg B100 stabilized with propyl gallate was taken in the holder and heating rate was adjusted 25°C/min from 25°C to 750°C and %mass loss was noted for comparing the thermal stability of both. As the temperature increases, the sample undergoes physical or chemical changes, which will be accompanied by mass loss. This method is used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in the inert atmosphere of Nitrogen, and the mass is recorded as a function of increasing temperature. Initial horizontal portion indicates the region where there is no mass change, which indicates the material is thermally stable. The slanting down portion indicates the mass loss. And it can be due to dehydration, decomposition or evaporation. From the % mass loss, the number of a molecule of hydrated water lost within the temperature range can be determined. Here the sample holder is attached to a thermos-balance which is highly temperature sensitive, so that whenever the temperature changes it automatically measures the mass of the sample. The temperature sensor records the sample temperature. The signals were amplified and recorded. The graphs obtained are % mass loss vs. temperature. Temperature is marked in abscissa and % mass loss in ordinate.

D. Results and discussion

1) Brake Thermal Efficiency

The variation of BTE with respect to load for different fuels (Diesel and Biodiesel with and without antioxidant) considered for the present analysis is presented in the figure No:1, BTE has the tendency to increase in power developed with an increase in applied load. This is due to the reduction in heat loss and increases in power developed with an increase in load. Biodiesel has low stability compared to the diesel, so some antioxidants are added to the

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biodiesel. Due to the ageing of the fuel and other oxidation processes, production of gum precipitates and there is the production of contaminants. But it is seen that the BTE is slightly less than the diesel. It's due to the low calorific value of the biodiesel. In order to prevent ageing and oxidations, antioxidants are added. The bio- diesel PG added 6 months is having highest efficiency among the biodiesel fuel. It's notable that all the bio-diesel with PG is superior to the pure biodiesel in the BTE.

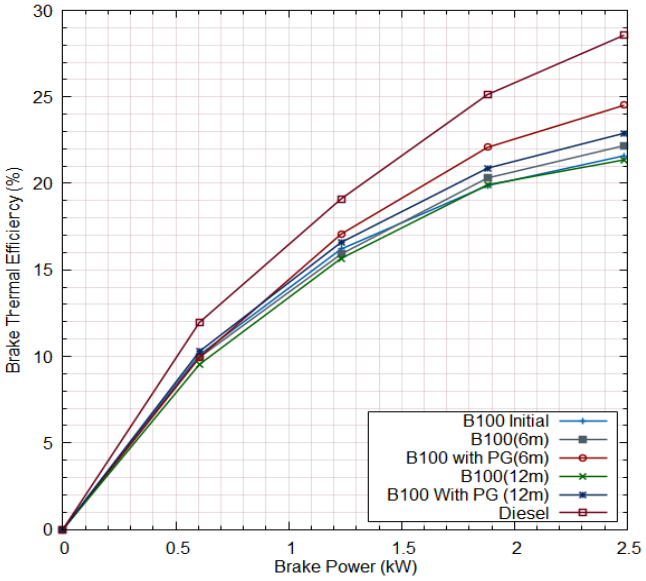

Fig. 2 Brake Thermal Efficiency vs Brake Power.

Maximum efficiency of the biodiesel is found to be 28.51 %. The low thermal efficiency of the biodiesel than the diesel is due to the higher calorific value of the diesel. Also, the bio diesel without PG (12 months) show very low BTE due to oxidation effects and Biodiesel with PG (6 months) show high BTE than pure Biodiesel. In general, for the long use and for storage, the break thermal efficiency of biodiesel can be increased by adding antioxidants.

2) Specific Fuel Consumption

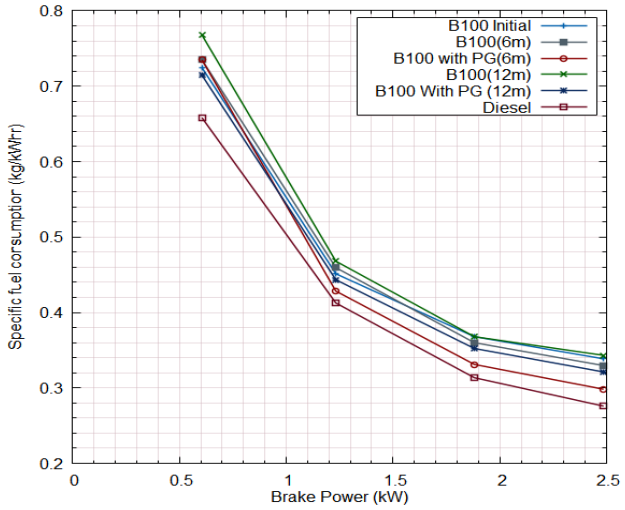

Fig. 3 Specific Fuel Consumption vs Brake Power.

The fuel consumption and the evaluation of fuel cost is an important factor considered to have an indication of the relative economy of the engine under test when compared with test results on the other engines. The criterion for economic power production is the specific fuel consumption which is the ratio of the mass of fuel required to be

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supplied to an engine to develop unit power per hour. Specific fuel consumption is less for the diesel as expected as they are having the highest calorific value than the biodiesel. From the graph, it's found that the initial biodiesel is having the highest specific fuel consumption. Even though the SFC of the biodiesel samples has an almost similar trend as that of diesel. It's a notable result that the biodiesel with PG after 6 months has a comparable trend as that of diesel. And very higher SFC is observed for the biodiesel without PG 6 months. So, it's a clear information about the effect of the oxidation of biodiesel. In the graph, the increasing pattern of the SFC is very clear, that means the oxidation and stability plays a vital role in the performance of the biodiesel.

3) Volumetric efficiency

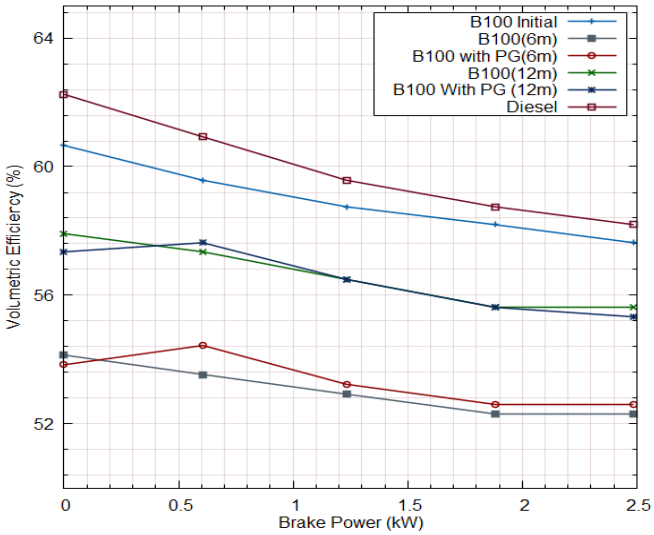

Fig. 4 Volumetric Efficiency vs Brake Power.

The engine output depends upon the maximum amount of charge taken in during the suction stroke. Volumetric efficiency is defined as the ratio of the actual volume of the charge drawn in during the suction stroke to the swept volume of the engine. Volumetric efficiency gives a limit on the amount of fuel which can be efficiently essentially an indication of the breathing capacity of the engine and it is burned in an engine because power output is proportional to the amount air sucked during suction. Average value of volumetric efficiency of an engine ranges from 70 to 80 percent Since diesel contains no inherent oxygen, it requires more air to burn, but for the case of biodiesel there is an excess amount of inherent oxygen in it and this is enough to burn the biodiesel. The maximum volumetric efficiency of biodiesel is found to be 60.65 %. The general trend of the volumetric efficiency is decreasing with the load. Diesel shows high volumetric efficiency and Biodiesel after 6 months shows very low volumetric efficiency. Biodiesel with and without PG shows similar characteristics in the volumetric efficiency.

E. Emission Test

1) Carbon monoxide

The CO emission increases as the air fuel mixture become rich, due to the inadequate amount of oxygen in the mixture to burn the fuel completely. Usually at the time of starting and idling the mixture will be rich and thereafter the mixture become lean for the part load. And also, when the engine runs above its half load the temperature in the cylinder is high, which made the chemical reaction of fuel with oxygen be easier and combustion becomes a complete. The presence of low molecular compounds that affect the atomization process result in mixture that produce higher CO emission. It's also due to the poor mixing of the fuel with O2. Initial biodiesel has very low carbon emission compared to other fuels because of the inherent oxygen in it. Whereas the biodiesel with PG after 6 months shows maximum carbon emission. This can be attributed to the fact that the inherent oxygen molecules in the biodiesel are loss due to the ageing and storage by the oxidation process.

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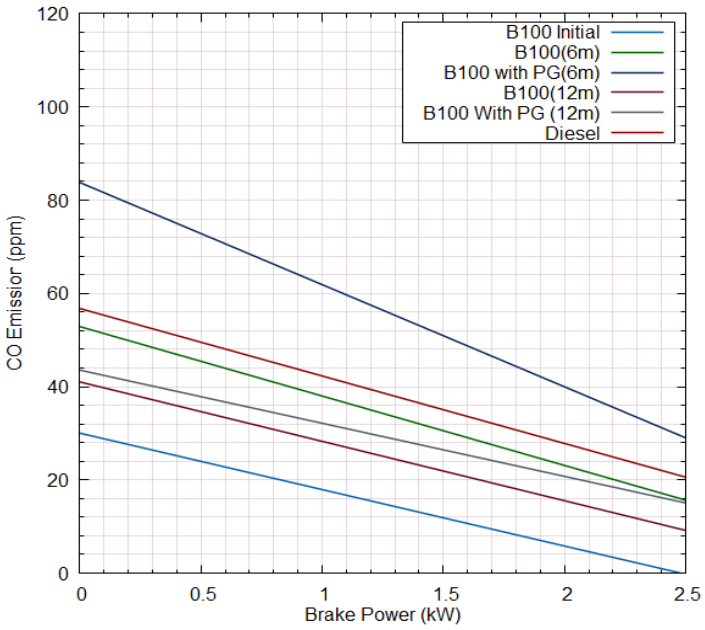

Fig. 5 CO Emission vs Brake Power.

2) NOx emission

Normally Diesel is emitting much for NOx which is a matter concern. But it's noticeable that the all biodiesel fuels emit a very low amount of NOx, and their trend for the NOx emission is not of much concern. The general trend of NOx emission is increasing with Brake power. But fortunately, all the biodiesel samples show a typically constant or decreasing trend apart from the normal diesel. The high NOx emission tendency of the diesel with high loads is also a parameter to the performance of the fuel. Initial Biodiesel and biodiesel with PG show constantly decreasing trend and other biodiesel samples also shows NOx emission below 20 ppm whereas the diesel shows very alarmingly high NOx emission.

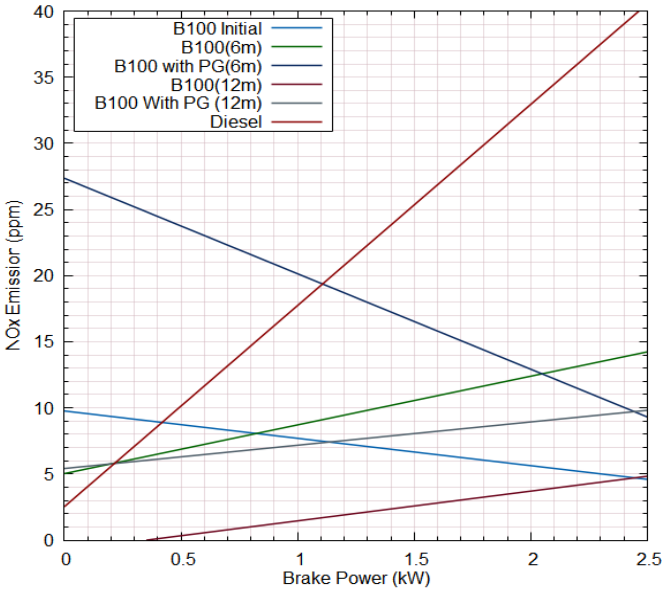

Fig. 6 NOx Emission vs Brake Power.

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II. THERMO GRAVIMETRIC ANALYSIS

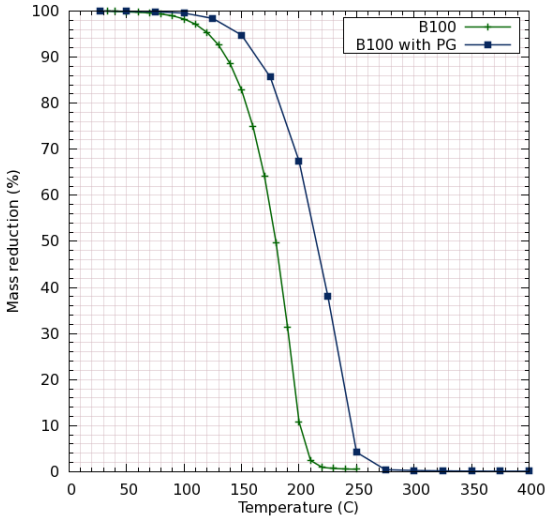

Fig. 7 Mass Reduction vs Temperature.

In B100 there is no appreciate mass loss up to 80°C from 33.85°C, which shows the horizontal portion. Up to 80°C B100 is thermally stable. After which the slope begins, which indicates the mass loss, that is due to dehydration, decomposition or evaporation. From the percentage mass loss, the number of molecules of hydrated water lost within the temperature range can be determined.

III. PAGE LAYOUT

An easy way to comply with the conference paper formatting requirements is to use this document as a template and simply type your text into it.

A. Page Layout:

Your paper must use a page size corresponding to A4 which is 210mm (8.27") wide and 297mm (11.69") long. The margins must be set as follows:

In B100 stabilized with antioxidant, there was no mass change from 27°C to 100°C that means it has more thermal stability. During that temperature, only a slight 9 decimal mass reduction occurred. From 100 to 250°C, slope indicated that most of the mass lost due to dehydration and decomposition or evaporation.Biodiesel with PG added has a slightly high temperature for volatilization. i.e. 200o C. but for the biodiesel without PG has a lower temperature for volatilization. i.e. 150oC. This implies that pure biodiesel without PG undergoes rapid volatilization at a lower temperature. But for the biodiesel with PG has a higher temperature for the volatilization. Thus, the biodiesel with PG is more stable at a higher temperature than the biodiesel without PG showing its stability with temperature. From thegraph, it's clear that the slope of the curve of Mass percentage vs Temperature of the Biodiesel without PG and the Biodiesel with PG aredifferent and the slope is more for the Biodiesel without PG. Which implies that Biodiesel with PG is more superior fuel than Biodiesel without PG.

F. Calculation of kinetic parameters from the TGA curves

The calculation kinetic data from the TGA curve is based on the formal kinetic equation

$$-\frac{dm}{dt} = f(m).k(T)$$

Where:
m: The actual mass of sample undergoing reaction
t: Time
k: Specific rate constant
T: Absolute temperature

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From the Arrhenius equation, the specific heat constant is calculated.

$$k = Ae^{-\frac{E_a}{RT}}$$

where:
A: The frequency factor
E: The activation energy
R: The molar gas constant

Assuming $f(m) = m^n$ The mass function depends on the reaction mechanism. Assuming $n = 1$ and rearranging the equation

$$-\frac{dm}{dt} = m^n . Ae^{-\frac{E_a}{RT}}$$

Taking natural log on both sides

$$\ln\left(-\frac{1}{m} \times \frac{dm}{dt}\right) = \ln A - \frac{E_a}{R} \ln \frac{1}{T}$$

1) B100 Coconut Oil Antioxidant stabilised

Comparing the equation of the liney $= -6.0806x + 6.7982$

$$R = 8.314\ J/mole.K$$

Thus $E_a = 6.0806 \times 8.314\ J/mole$
$E_a = 50.5541084$
$\ln A = 6.7982$
$A = e^{6.789}$
$= 888.02509\ s^{-1}$

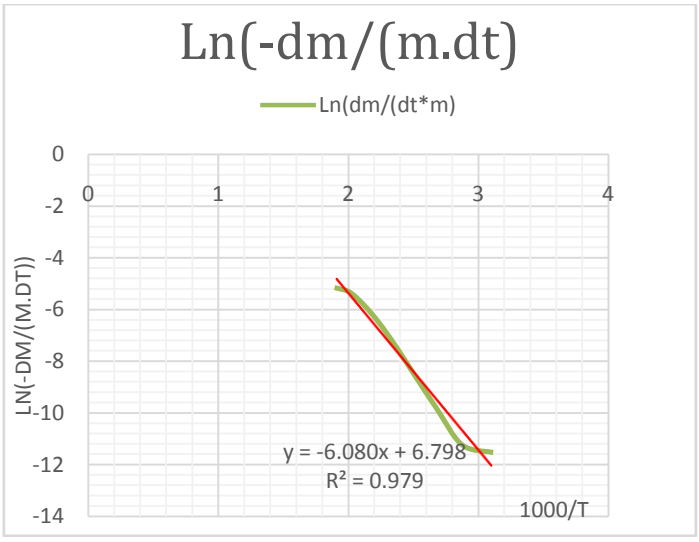

Fig. 8 Graph for B100 with antioxidant

2) B100 without antioxidant

Equation of the liney $= -5.8172x + 6.6929$
$E_a = 5.817 \times 8.314$
$E_a = 48.362538\ J/mole$
$\ln A = 6.6929$
$A = e^{6.6929}$
$A = 806.6581\ s^{-1}$

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From this, it is clear that thermal stability of antioxidant stabilised biodiesel is more than that of pure biodiesel.

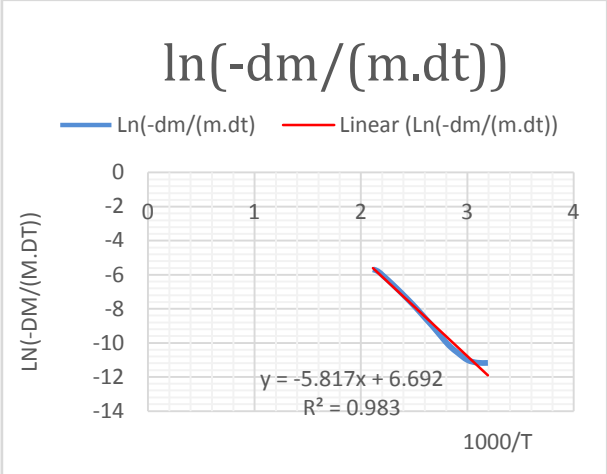

Fig. 9 Graph for B100 without antioxidant

IV. CONCLUSION

An experimental investigation was conducted with antioxidant stabilized biodiesel. Oxidative stability has to be considered as an essential characteristic in the control of the biodiesel properties. Biodiesel is also potentially subject to hydrolytic degradation, caused by the presence of moisture and light. In general, for the long use and for storage, the break thermal efficiency of biodiesel can be maintained by adding antioxidants. Also, shortage of diesel can be reduced by biodiesel from the edible or non-edible oils. Thermal stability of antioxidant stabilized biodiesel is greater than pure biodiesel. Even though the Calorific value of coconut oil bio diesel greater than that of diesel, BTE and specific fuel consumptions are less in biodiesel, hence separate fuel injector must be designed to get better values

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BIOGRAPHY

Ranjith B P received the B.Tech and M. Tech (Thermal science) degree in mechanical engineering the University of kerala, India, in 1995 and 2009. He is currently pursuing the Ph.D. degree in Kerala University. His current research interests include the combustion modelling, emission and thermogravimetric analysis of various biodiesel. He is currently working as HOD in mechanical engineering, Goverment polytechnic college, chelakkara.