Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 08, August-2016

Performance Study and Standardization of Oxidation Stability Test rig for Biodiesel

Manjunath V B
PG Student
Thermal Power engineering
VTU PG Studies
Mysuru, Karnataka, India,

S Shamsundar
Associate Professor,
Mechanical Engineering,
The National Institute of Engineering,
Mysuru, Karnataka, India,

M C Math
Associate Professor,
Thermal Power Engineering,
VTU PG Studies,
Mysuru, Karnataka, India,

Abstract*— The vegetable oils, animal fats and their biodiesel suffer with the drawback of deterioration of its quality when it comes in contact with the oxygen. Currently, Rancimat test [EN 14214] method and Petroxy [ASTM 6751 – 07b] methods are used to find the oxidation stability of biodiesel. In this research project, a new oxidation stability test rig is designed and fabricated by considering Rancimat test, Petroxy and DGMK714 methods as the reference standard methods. The scope of the work is to produce a cost effective new oxidation stability test device for testing biodiesel and standardize the product and procedure. Experiments have been conducted on a new test rig by using biodiesel samples and results have been compared with standard Petroxy test rig. The test procedure and initial conditions for new test rig is made similar to the Petroxy test by maintaining the constant temperature at 140^{0}C and pressure at 7 bar. In this work, compressed air is replaced by oxygen. The Pongamia pinnata and coconut biodiesel are used for experimentation. The *tertiary butyl hydroquinone* (TBHQ) antioxidant is used for enhancing the oxidation stability of the biodiesel. The oxidation stability of 169min. and 125min. in the new test rig was obtained as compared to 138.21min and 88.36min in Petroxy test ring for Pongamia pinnata and coconut biodiesel respectively with antioxidant. The tests have been repeated without using TBHQ and the oxidation stability has decreased drastically to 52min. and 38min. in new test rig for both the test sample. Results indicate that there is a marked increase in oxidation stability when antioxidant is used for both the samples in new test rig and Petroxy test rig.

Keywords*— Oxidation Stability; Pongamia pinnata; Coconut Biodiesel; TBHQ; New Test rig; Petroxy;

I. INTRODUCTION

Biodiesel represents an alternative to petroleum-based diesel fuel and it consists of mono-alkyl esters of fatty acids, extracted from plant oils and animal fats [1]. Biodiesel provides engine performance similar to that obtained with diesel fuel. India can produce about 4 – 5 million tons per year of biodiesel, which is about 10% of current diesel demand. In Karnataka bio-fuels production from non-edible oil initiated by the Karnataka government and Karnataka state bio-fuel information and demonstration center is taking much interest in bio-fuel and initiated bio-fuel production and R&D center in every district of Karnataka. KSBF I&D center is funding NIE-CREST for generation of biodiesel, conducting the awareness programs to educate the formers. But apart from all these advantages Biodiesel has some serious drawbacks, and problems compared to conventional diesel oil. One of the important drawbacks is the oxidation stability. The oxidation stability of the biodiesel is defined as the ability of the biodiesel to resist the oxidative degradation when contact with oxygen [3]. It has direct impact on the storage capacity of the biodiesel. The thermal stability also affects the storage stability of the biodiesel. The thermal degradation of biodiesel occurs due to formation of sediments and deposits during the storage by the effect of temperature [2]. The thermal stability of the biodiesel is important factor to know the quality and performance along with the oxidation stability. The new standard test method is required to find the oxidation stability and thermal stability of biodiesel [3]. Hence, in this research an attempt has made to develop an innovative device and method to find the oxidation stability.

A. Oxidation Stability of Biodiesel

The long chain free fatty acid ester is present in biodiesel due to presence of unsaturated fatty acids in vegetable oils and animal fat [5]. FFA accelerates the oxidation when oil is exposed to air and high temperature during storage which may yield the polymerized compounds. Auto oxidation of biodiesel causes degradation of fuel quality by affecting the stability parameters [6].

Initiation

$$RH + I \longrightarrow R^* + IH$$

Propagation

$$R + O2 \longrightarrow ROO^*$$

$$ROO^* + RH \longrightarrow ROOH + R^*$$

Cycle repeats

Termination

$$R^* + R^* \longrightarrow R - R$$

$$ROO^* + ROO^* \longrightarrow \text{Stable product}$$

Figure 1: Oxidation chemical reaction in biodiesel [1] [2]

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 08, August-2016

Figure 1 indicates that, oxidation reaction in biodiesel gives out by-products like alcohols, aldehyde, shorter chain of carboxylic acids and gum like sediments. It results in blocking the fuel filter and fuel injection nozzle, deposits formation in the combustion chamber of the engine and other components of fuel supply system [7]. Therefore, oxidation stability is an important parameter for addressing the quality and purity of biodiesel. The oxidative degradation of biodiesel can be controlled by the addition of antioxidants [8] [10].

B. Existing Standard Test Methods

1) Rancimat Test [EN 14214]

The Rancimat test has two methods; one is long term storage stability test and other one is rapid acceleration oxidation stability test. Oxygen is passing continuously to the sample at the rate of 20 liters per hour and maintaining constant temperature at 110^0C. The free fatty acids are oxidized during the reaction with oxygen [3]. The volatile and secondary reaction products are formed at the end of the experiment and transferred into the measuring vessel by the air stream and absorbed from measuring solution. It increases the volume of solution due to the absorption of by-products of oxidation reaction [2] [9]. At a particular time, the conductivity of biodiesel suddenly increases due to oxidation reaction. The time duration from starting of experimentation to the point of sudden rise in the conductivity of biodiesel is considered as oxidation stability. The Standardized oxidation stability period of biodiesel is 6hr [3] [5].

2) Petroxy Test [ASTM 6751 – 07b]

The Petroxy test method is used to find the oxidation stability of biodiesel, lubricant oil and conventional diesel. This equipment has 20ml capacity reactor in that 5ml sample is generally taken for experiment. The oxygen supplied to the reactor at 7bar pressure and then starts the experiment by heating upto constant temperature at 1400C. The expansion of oxygen molecule due to heat input leads to the increase in the pressure in reactor. The termination of the experiment is generally done when pressure drops 10% of the maximum pressure [4].

II. OXIDATION STABILITY TEST RIG AND METHODOLOGY

The new oxidation stability unit has test rig set-up and automated control system. These two are important parts of this experiment. In reactor set-up, reactor shell is the main part in which the biodiesel sample is poured to find oxidation stability. This reactor design is done based on the DGMK 714 standards. Figure 2 shows the 3D model of the designed test rig which is generated by using CATIA V5R20 software. The maximum working pressure of the reactor is determined by using longitudinal stress formula. The heating of biodiesel is done by induction heating band which is controlled continuously to maintain the temperature at 140^0C till the completion of the experiment.

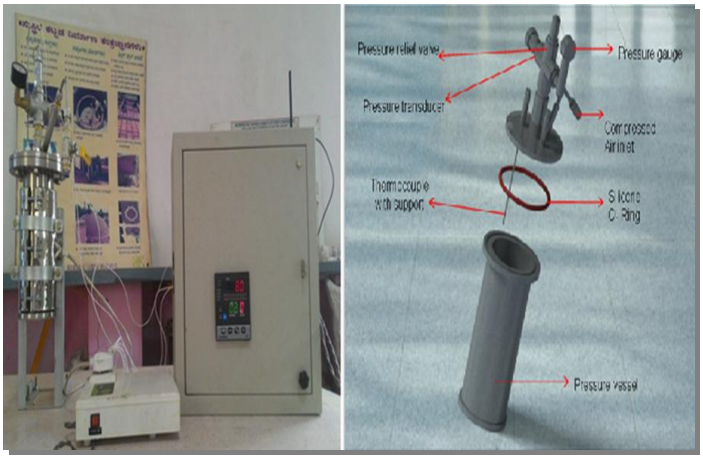

Figure 2: a) Fabricated oxidation stability test rig. b) Designed 3D model of the reactor unit in CATIA V5R20

The pressure relief valve is used for safety purpose which maintains the compressed fluid pressure within predetermined working pressure of the reactor. If pressure is more than predetermined pressure then, relief valve is opened and excess pressure went out by auxiliary path from the reactor. The capacity pressure relief valve is 10 and the working pressure of test rig is 7bar.

A. Control System and Monitoring system

In this work, temperature monitoring system and pressure monitoring system control systems are used. Thermocouple and relay circuit is used for temperature monitoring where thermocouple sense the change in temperature and sends analogue signal to signal conditioner to covert from an analogue input to digital output which is fed to MODBUS. The control system maintains constant operating temperature in reactor. In pressure monitoring system, the pressure transducer senses the pressure inside the reactor and sends analogue signals to the signal conditioner for getting the output digital values.

The both monitoring systems are programmed in the microcontroller 8028 which is flexible configuration option for 8 channels accepting universal input and 4 relay to serve these applications. This unit has separate Numeric display for group and process values. Figure 3 shows the automatic controlling and monitoring system.

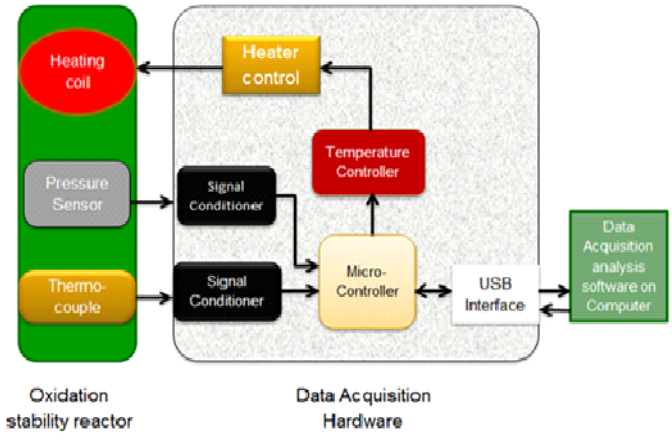

Figure 3: Block diagram of Automatic Control and Monitoring system

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 08, August-2016

III. METHODOLOGY AND TEST PROCEDURE

The design and development of the new oxidation stability test rig is done by following the working principle of existing standards like Petroxy and Rancimat oxidation stability test methods. Particularly, it works on the basis of Petroxy [ASTM 6751 07b] test method [4]. The test procedure, initial conditions and co-relations of the Petroxy test are followed. The main difference is the use of quantity of sample for the test. In Petroxy test, 5ml of biodiesel sample is used for the test but in this new test rig, 215ml of biodiesel is used. The reactor is designed for 1:3 ratios (i.e. volume fraction of bio-fuel to the oxygen) to be filled in the reactor. The ratio is decided by taking rotating bomb oxidation test method and the Petroxy test method as the reference [6].

Initially, preliminary tests have been conducted with Pongamia pinnata biodiesel by maintaining a pressure at 5bar and temperature at 110^{0}C. These test conditions are not matching with the standard Petroxy test method. During this test, compressed air is used.

The main objective of this work was the standardization of the test rig. Hence, standard test conditions like 7bar pressure and constant temperature of 140^{0}C. In addition, pure oxygen is supplied to reactor shell which clears the path for standardization [4].

3.1 Experiment Procedure

In this work, the standard Petroxy test procedure is followed to find the oxidation stability of the test sample to compare the results with Petroxy test methods.

IV. RESULT AND DISCUSSION

A. Initial Experiment and Results

Pongamia pinnata and coconut biodiesel with and without TBHQ antioxidant samples are prepared for the experiments. The experiment of both biodiesel samples was conducted as per test procedure by supplying compressed oxygen to the test rig. The samples are tested in new test rig and Petroxy test rig. Figure 4 shows the comparison of oxidation stability between Pongamia pinnata biodiesel at 110^{0}C constant temperature and compressed air supplied at 5bar pressure and Pongamia pinnata biodiesel at 140^{0}C constant temperature and compressed oxygen supplied at 7bar.

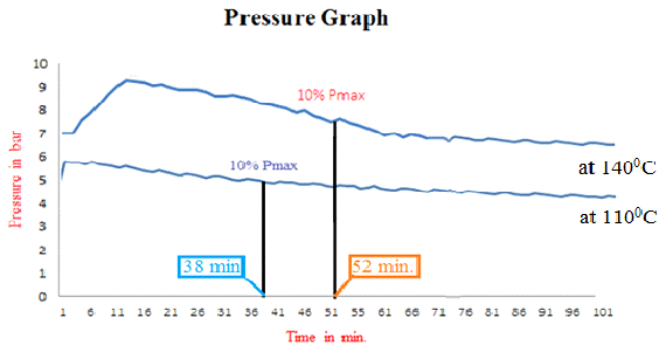

Figure 4: Comparison of oxidation stability at different test parameters

The results indicate that there is 26.9% increase in oxidation stability for Pongamia pinnata biodiesel under 140^{0}C constant temperature and compressed oxygen supplied at 7 bar pressure test conditions as compared to 110^{0}C constant temperature and compressed air is supplied at 5 bar pressure test conditions as shown in Figure 5. It may due to increase in operating temperature and pressure and supply of oxygen.

Figure 5, indicates the results of Pongamia pinnata and coconut biodiesel without antioxidant when test was conducted in new test rig and in standard Petroxy test method. The variation can be noticed between new test rig results and Petroxy test rig results. The variations in the results occur due to convective heat transfer between reactor shell and the biodiesel sample. It results in inaccurate maintenance of the constant temperature in new test rig.

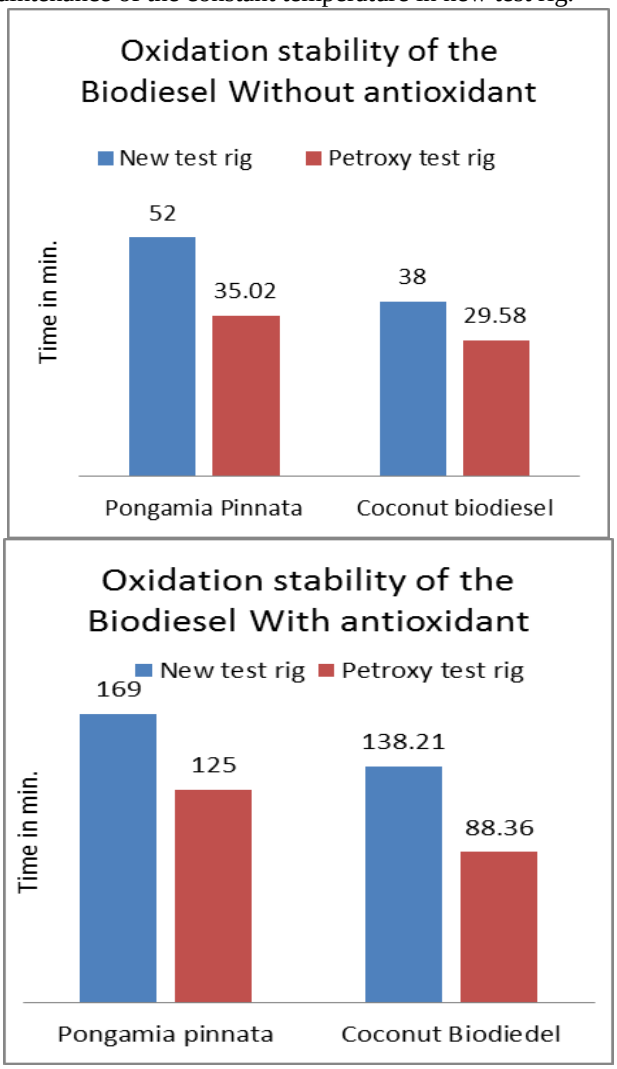

Figure 5: Oxidation Stability of the biodiesel in new test rig and in Petroxy test rig a) without antioxidant sample b) With antioxidant sample

Table 1 shows results of the oxidation stability of biodiesel without adding TBHQ antioxidant and comparison is made with the standard Petroxy test rig. The results of Pongamia pinnata and coconut biodiesel in new test rig was 52 min. and 38 min respectively and the oxidation stability of same biodiesel samples in Petroxy test rig are 35.05 min and 29.58 min. respectively. The variation of the result occurs due to high rate of heat transfer between steel reactor shell and biodiesel. It may due to difficult in maintaining the constant temperature.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 08, August-2016

Experiment on Oxidation stability of Biodiesel with antioxid*ant*				
Particulars/Properties	Pongamia pinnata		Coconut biodiesel	
Test rig used	On New test rig at NIE-CREST	On Petroxy test at HPCL	On New test rig at NIE-CREST	On Petroxy test rig at HPCL
Temperature maintained	140^0C	140^0C	140^0C	140^0C
Pressure Provided	7 bar	7 bar	7 bar	7 bar
P_{max} Obtained during experimentation	9.58 bar	9.99 bar	9.38 bar	11.24 bar
Supply	Oxygen	Oxygen	Oxygen	Oxygen
Oxidation stability obtained	52 min.	35.05 min	38 min.	29.58 min.

The Pongamia pinnata and coconut biodiesel with antioxidant samples are tested in new test rig and in Petroxy test rig. The results are shown in Table 2. The results of Pongamia pinnata and coconut biodiesel in new test rig was 169 min. and 125 min respectively and the oxidation stability of same biodiesel samples in Petroxy test rig are 138.21 min and 88.36 min. respectively. The variation of results between new test results and Petroxy test results can observe.

Table 2: Experiment on Oxidation stability of Biodiesel with antioxidant

Particulars / Properties	Pongamia pinnata		Coconut biodiesel	
Test rig used	On New test rig at NIE-CREST	On Petroxy test at HPCL	On New test rig at NIE-CREST	On Petroxy test rig at HPCL
Temperature maintained	1400C	1400C	1400C	1400C
Pressure Provided	7 bar	7 bar	7 bar	7 bar
Pmax Obtained during experimentation	9.59 bar	10.70 bar	9.48 bar	9.86 bar
Supply	Oxygen	Oxygen	Oxygen	Oxygen
Oxidation stability obtained	169 min	138.21 min	125 min	88.36 min

The oxidation stability of biodiesel was improved by adding the additives like antioxidants. TBHQ antioxidant was used to prevent the oxidation of biodiesel mean while it increases the stability. The biodiesel with antioxidant sample was prepared by considering the optimum amount of antioxidant per liter of biodiesel and mixed using magnetic stirrer.

The oxidation stability of Pongamia pinnata and coconut biodiesel without antioxidants results in new test rig are 52 min. and 38 min. and with antioxidant results are 169 min. and 125 min. respectively as shown in the Figure 6. The results indicate 69.23% of increase in oxidation stability of Pongamia pinnata and 69.6% of increase in oxidation stability of coconut biodiesel when adding antioxidant.

ACKNOWLEDGMENT

The authors would like to express their appreciation to the "Karnataka state biofuel Information and Demonstration center'' Government of Karnataka for provides funding to carry-out this research work. The authors also express their appreciation to the HPCL green R&D center, Bengaluru, Karnataka, India for their support to conduct the experiments at their crude oil lab.

CONCLUSION

The new oxidation stability test rig design and fabrication was done to conduct experiment on Biodiesel. The automation system was developed to control and monitoring the oxidation stability test rig and also access the readings. The similar test procedure and preconditions setup was done for conducting the experiment and standardizing the new oxidation stability test rig. The test procedure was maintained as same in the Petroxy test method using samples of Pongamia pinnata and coconut biodiesel. The experimental oxidation stability of 169min. and 125min. in the new test rig was obtained as compared to 138.21min and 88.36min in Petroxy test ring for Pongamia pinnata and coconut biodiesel respectively with antioxidant. The tests have been repeated without using tertiary butyl hydroquinone (TBHQ) and the oxidation stability has decreased drastically to 52min. and 38min. in new test rig for both the test samples. Results indicate that there is a marked increase in oxidation stability when antioxidant is used for both the samples in new test rig and Petroxy test rig. The experiment test results with Petroxy test and new test rig are shown variations due to inconsistent in maintaining the constant temperature. This occurs due to convective heat transfer from reactor shell to biodiesel sample even cut-off the heating coil power and lack of accuracy in controlling and monitoring constant temperature of the system.

REFERENCE

[1] Stability studies of bio-diesel, by E. Natarajan, Mechanical engineering Department, Anna University, Chennai. IJES Vol. 2 Iss. 4 2012 PP. 152 – 155.
[2] Comparative Studies of Oxidative Stability Properties of Biodiesel Produced from Azadirachta indica and Hevea brasiliensis seeds. Greener Journal of Agricultural Sciences, ISSN: 2276-7770, Vol. 2 (5), pp. 195-206, September 2012.
[3] Review of different test methods for the evaluation of stability of biodiesel, by Siddharth Jain and M.P. Sharma, IIT Roorkee, RSER 14 (2010) 1937–1947.
[4] Standard test method for oxidation stability of middle Distillate fuels, Rapid scale oxidation test in Petroxy D7545 – 14.
[5] Oxidation stability of biodiesel fuels and blends using the Rancimat and Petroxy methods. Effect of 4-allyl-2, 6-dimethoxyphenol and catechol as biodiesel additives on oxidation stability. Chemical Engineering July 2014, Volume 2, Article 43.
[6] Oxidation Stability of Inhibited Mineral Insulating Oil by Rotating Bomb -Method Of Test, UDC 621.315.615~2 : 543.872, IS 12958: 1990
[7] Study of oxidation stability of Jatropha curcas biodiesel and diesel blends, International Journal of Energy and Environment, Volume 2, Issue 3, 2011 pp.533-542.
[8] Accelerated Oxidation Processes in Biodiesel, by M. Canakci, A. Monyem, J. Van Gerpen, American Society of Agricultural Engineers 0001-2351 / 99 / 4206-1565 VOL. 42(6): 1565-1572.
[9] Animal and Vegetable fats and oils, Determination of oxidation stability by accelerated oxidation test, Ethiopian standard ISO 6886:2012.
[10] Effect of Oxidation Under Accelerated Conditions on Fuel Properties of Methyl Soyate, by Robert O. Dunn, Oil Chemical Research, USDA, ARS, National Center for Agricultural Utilization Research, Peoria, Illinois Jaocs, Vol. 79, no. 9 (2002).