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OXIDATION STABILITY OF MUSTARD METHYL ESTER: BIODIESEL MADE FROM WASTE MUSTARD OIL

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ABSTRACT

As the demands of Fossil fuel are increasing day by day, The Modern civilization is concentrating on the latest technologies to Conserve Fossil fuels. Biodiesel, defined as monoalkyl ester derivatives of long chain fatty acids, can be used as an alternative to Diesel. Oxidation Stability of Biodiesel tells about the quality of synthesized biodiesel. Thus Biodiesel was synthesized from waste Mustard oil by Transesterification Process and its Oxidation Stability was checked in Professional Biodiesel Rancimat 893 according to EN-14112 Specifications. Biodiesel Made from waste Mustard oil has showed an effective Oxidation StabilityThe Oxidation Stability of Mustard Methyl Ester has come to be 5.7 hours respectively.

Keywords—Biodiesel, Mustard Oil, Diesel, Renewable Energy, Mustard Methyl Ester.

I. INTRODUCTİON

As the Fossil fuel is declining day by day and the demands of fuel from alternative resources are increasing rapidly, Biodiesel is one of Alternative fuel. Acid-catalyzed biodiesel production processes is a competitive alternative for biodiesel production using waste cooking oil as raw materials and are less complex than alkali-catalyzed approaches. As consumption of fossil fuels increasing day by day, the quantity of fossil fuel is decreasing rapidly and the price of fuel is also rising day by day [1].

Biodiesel is alternative to the conventional petroleum fuel and is made by mono-alkyl-esters of long chain fatty acids derived from vegetable oils or animal fat[2]. Biodiesel generally can synthesized from available vegetable oils like palm, soybean, peanut, sunflower, rape, coconut, karanja, neem, cotton, mustard, Jatropha, linseed and castor through a chemical process known as transesterification [3-5] Biodiesel is commercially produced through the transesterification of various types of oils like vegetable oils, used frying oils and many other varieties of Oils [6]. Biodiesel is obtained by the chain reactions of oil and methanol or ethanol in the presence of an catalyst like KOH, NaOH or H2SO4 [7]. There is a large number of vegetable oil that are being used as an alternative to biodiesel in various countries like soybean oil is being used in U.S.A., palm oil in Malaysia and Indonesia, rapeseed and sunflower oil in Europe and coconut oil is being used widely in Philippines [8]. Biodiesel as an alternative fuel can be used in various diesel engines in pure form (B100) or it can be blended

with petroleum diesel in various concentrations and Ratios like B10, B20, B30, B40, B50, B60, B70, B80 and B90 [9].

Biodiesel is biodegradable in Nature and environment friendly fuel but due to the reason that it is unstable in nature and can loss its quality and properties over time, thus Oxidation stability is most necessary parameter of biodiesel. The oxidation stability of biodiesel is always lower than that of petroleum-based diesel. Fatty wastes in oil cause more oxidation because they vary in level of unsaturation. This leads to generation of more carbon-carbon double bonds and fewer hydrogen molecules on the fatty acid chains. When Biodiesel is kept in presence of Oxygen, It easily got oxidized as the oxygen is rapidly attached to the alkyl group in Biodiesel. [10]. So, Oxidation Stability plays an important role in the quality of Biodiesel.. Thus Mustard Biodiesel from Waste Mustard oil was synthesized and its Oxidation Stability was checked by using Professional Biodiesel Rancimat 893. So, below is the full paper representing the various methods and conclusions.

Table 1. Physico-Chemical Properties and Standards of Biodiesel in Accordance with ASTM D-6751, EN-14214, and IS-15607 Standards: [12][13]

Property	ASTM D 6751 test method	ASTM D 6751 limits	EN 14214 test method	EN 14214 limits	IS 15607 test method	IS 15607 limits
flash point (C)	D-93	min.130	EN ISO 3679	min. 120	IS 1448 P:21	min. 120
viscosity at 40 C (cSt)	D-445	1.9-6.0	EN ISO 3104	3.5-5.0	IS 1448 P:25	2.5-6.0
sulfated ash (% mass	D-874	max. 0.02	EN ISO 3987	Max. 0.02	IS 1448 P:4	Max. 0.02
sulfur (% mass)	D-5453/ D-4294	max. 0.0015 (S 15) max. 0.05 (S 500)	EN ISO 20846/20884	Max. 0.0010	ASTM D 5453	Max. 0.005
copper corrosion	D-130	max. 37	EN ISO 2160	max. 1	IS 1448 P:15	max. 1
Cetane number	D-613	min. 47	EN ISO 5165	min. 51	IS 1448 P:9	min. 51
Water and sediment (vol. %)	(vol. %) D-2709	max. 0.05			D-2709	Max. 0.05
Conradson carbon residue (CCR) 100% (% mass)	D-4530	Max. 0.05	EN ISO 10370	Max. 0.3	D-4530	Max. 0.05
Neutralization value (mg, KOH/g)	D-664	Max. 0.50	EN ISO 14104	Max. 0.5	IS 1448 P:1/sec:1	Max. 0.50
free glycerin (% mass)	D-6584	max. 0.02	EN ISO 14105/14106	max. 0.02	D-6584	Max. 0.02
total glycerin (% mass	D-6584	max. 0.24	EN ISO 14105	max. 0.25	D-6584	max. 0.25
phosphorus (% mass)	D-4951	max. 0.001	EN 14107	max. 0.0010	D-4951	max. 0.001
distillation temperature	D-1160	90% at 360 C			not under spec.	min 90%
oxidation stability at 110 C (h)	EN 14112	Min. 3 hr.	EN ISO 14112	Min 6 Hr.	EN 14112	Min. 6 h.
CFPP(°C)	D-6371		EN 116	Variable	IS 1448 P1:10	

II. MATERIALS

Waste mustard oil is used for transesterification reaction so that to use the waste in the formation of useful energy. This oil is used for many cooking processes and then the Waste Mustard oil is collected. The Chemicals used in this experiment are Methanol and a Catalyst used is Potassium hydroxide This KOH used in this experiment is in solid state i.e. in form of pallets. For the determination of acid number, Isopropyl alcohol was used in which Phenolphthalein was used as an indicator in the titration..

III. METHODS

In Sthis process the ester is produced when vegetable oil combines with a simple alcohol in presence of a catalyst. The fatty acids of vegetable oil exchange places with the (OH) groups of the alcohol producing glycerol and methyl, ethyl or butyl fatty acids ester depending on the type of alcohol used. The concentration of catalyst can affects the level of ester recovery and requires experimental optimization as concentration of catalyst is less than required value reaction will not complete. Its excess quantity can lead to soap formation. [14].

The Alcohol used in this process is mainly 15 % of mass of Oil and the Catalyst used may vary from 1% to 2% of Mass of oil respectively. Mainly, Methanol or Ethanol is used as Alcohols and potassium Hydroxide is used as catalyst. NaOH can also be used but According to some scientific reasons of effect of Na ions on Biodiesel, mostly KOH is used. [15].

3.1 Free Fatty Acıds

Free Fatty Acids (FFA) composition in any vegetable oil plays an important role in synthesis of biodiesel. The presence of too high level of free fatty acids will retard or stop the transesterification reaction. To ensure a successful conversion to bio-diesel, determining the exact amount of catalyst needed to neutralize KOH/gm acids by performing a titration test is worthwhile. Adding too much catalyst will result in excessive amounts of soap in the final bio-diesel product. If too little catalyst is added, transesterification will not occur. So, the more will be free Fatty Acids in oil, the lesser will be the desired product. In other words, The Free Fatty Acid number must be lie between 1% to 2.5%. For Mustard Oil, the free fatty Acid Number was 1.9. In general, FFA = 2 X ACID NUMBER. So, To Find Acid number in vegetable oil, pour 3 gram of Oil in a beaker and Add 50 mL Isopropyl Alcohol. After it, pour potassium hydroxide Normality N/10 solution in the burette. Now add 3-5 drops of Phenolphthalein indicator and titrate against KOH till the color changes to pink. Note Amount of KOH used. And by applying the Formula of Acid number, we can easily find out FFA of that Oil. 12

3.2 Transesterıfıcatıon Process

The Transesterification is widely used process for the synthesis of biodiesel from oil. In this process, when we Mix Oil with alcohol in the presence of Catalyst, The formation of Alkyl ester and Glycerin takes place. Alkyl ester is the desired product and is considered as Biodiesel whereas glycerin is waste product in this reaction and can be used to make soap [16]. So, firstly the oil to be synthesized into biodiesel is heated to 60°C temperature. In this Meantime, Alcohol is mixed with catalyst (KOH) till the perfect solution is made. After Achieving the

desired Temperature, The Alcohol and Catalyst solution is poured into the oil and leaved for one hour with continuous steering at constant temperature (60°C). At this meantime, the following reaction takes place:

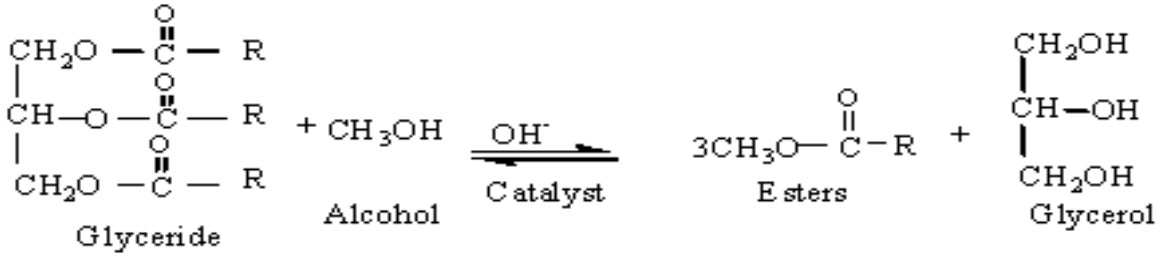

Fig. 1: Transesterification Reaction

In many Research papers, the time for Steering is advised for Two Hours but According to this Experiment, It is observed that the reaction is completed in only one hour. After this continuous steering for 1 hour, the Mixture is poured into separation flask and allowed to settle for 12 hours. After the period of 12 hours, Alkyl ester and glycerin will got separated..

3.3 Separatıon

After the Settle time of 12 hours, the alkyl esters and glycerin get separated and the glycerin is removed from the separation flask from the downward Tap. This glycerin is a component of soap and can be used in soap Synthesis in further different Methods. The alkyl ester is preserved for further processes.

Fig.1. Separation of Mustard Methyl Ester and Glycerin

3.4 Washıng Process

The Water Wash is most important process in the synthesis of biodiesel. Water washing is used to remove impurities and tiny particles from the alkyl esters. Mainly, Water is used for washing because water has very high tendency to combine with the impurities and other particles which may create problem to the alkyl esters. Majority of the researchers use simple water Washing. In this process, the water is heated to 45°C and is mixed with the Alkyl ester in separation flask. After 2 hours, the impurities are entrapped with water and this water becomes milky. The milky water is removed by the exit tap of separation flask. This process continuous till the transparent water is obtained at the bottom of separation flask.

3.5 Heatıng

In Water washing, all the water drops cannot be removed from exit Tap. Some drops of water get mixed with Alkyl ester. As we know that the boiling point of Water is 100°C and that of Methanol or Ethanol is 60°C. So, Alkyl esters are heated and Stirred at the Temperature of 110°C so that to remove all unwanted particles available in Biodiesel. After Heating, the Liquid obtained is called Biodiesel and can be used for further studies of Stability and other Engine Studies.

IV. EXPERIMENTAL SECTION

4.1 Materıals and Method

The waste Mustard oil was collected from the Home Based Cooking and was filtered to remove several impurities. Then Mustard Oil was poured in a Beaker and was heated to 60°C by using Digital Heater and Magnetic Stirrer. In the Meantime, 1.5% KOH was mixed in 15% methanol and the Solution was poured into the Beaker. After then, the whole Solution was supposed to be at constant temperature and continuous steering for One hour. After continuous steering for one hour, the solution was poured into Separation flask and the solution was not disturbed for 12 hours so that Mustard Methyl ester [MME] and glycerin settled to their respective places.

After 12 hours, the glycerin was removed from the exit tap of Separation flask and the remaining Mustard Methyl ester was kept in separation flask for further processes.

The obtained Mustard Methyl Ester was washed with heated water (45°C) four times till the transparent water was not obtained. After this Process of 6 hours, The Mustard Methyl ester was poured into a beaker and was again heated at the temperature of 110°C so that to remove water and methanol from the MME.

Thus after the series of processes, The Mustard Biodiesel made from Water Mustard Oil was obtained as a final product

4.2 Bıodıesel Stabılıty Testıng

As the Oxidation of biodiesel is very big problem in storing the biodiesel for a long time [11], thus the Oxidation stability of every freshly synthesized biodiesel is checked using electrical instrument called Profession Biodiesel Rancimat. This is most efficient device to check the oxidation stability of every Biodiesel.

Oxidation Stability of biodiesel was studied in the Rancimat equipment model 893 (Metrohm, Switzerland), according to EN-14112 specifications [17]. The Biodiesel made from used mustard Oil was tested and it showed an effective Oxidation Stability of 5.7 Hours. The Rancimat method is also called the automated swift test and

automated version of the previously used and extremely complicated, labor-intensive and time consuming Active Oxygen Method. In the Rancimat Method, the oxidation is induced by passing a stream of air at the rate of 10 L/h through biodiesel sample (3 g), kept at constant temperature 110°C. The vapours released during the oxidation process, together with the air, are passed into the flask containing 50 mL of triple Deionized water, and contain an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicates the end of IP when the conductivity begins to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. When the conductivity of this measuring solution is recorded continuously, an oxidation curve is obtained whose point of inflection is known as the IP or oil stability index. The Principle Diagram of Rancimat is as followed:

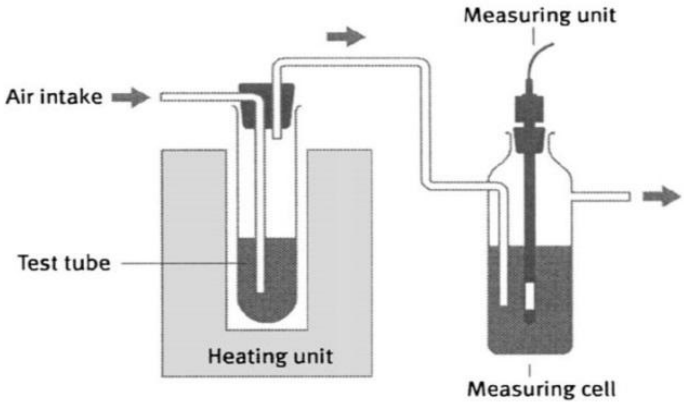

Fig.2. Principles of Measurement of the Rancimat Test Method (EN-14112/IS-15607).[11]

The 3 gram sample of Mustard Methyl Ester was poured into test tube and the apparatus was started for the results of Oxidation Stability of MME. After the time period of 6 hours, the Mustard Biodiesel was oxidized in the Professional Biodiesel Rancimat. Below is the graph obtained from Stabnet Software of Professional Biodiesel Rancimat Showing the Oxidation Stability.

V. CONCLUSION

An alternative method to the one accepted by standard EN14214 is used for studying the oxidation stability of biodiesel. The results obtained by this method, Mustard Biodiesel, showed the positive results as Oxidation Stability is came to be 5.7 Hours. So this OS is fulfilling the three major Standards as American Standard, Europe Standard and Indian Standard using the 14112 standard, the Rancimat method. If the Oxidation stability will be more, The Efficiency and Quality will also be good. As, the Oxidation stability of Mustard Methyl ester is 5.7 h, the prepared sample meets the requirements of IS 14112 Standard of Biodiesel. So, Mustard Biodiesel can be used as an alternative to the Petroleum Diesel as it fulfills the ASTM D 6751 limits of Oxidation Stability of minimum 3 hours. But it not satisfies Indian Standards and European standards for Oxidation Stability of Minimum 6 Hours. Thus by using Antioxidants like Tert-butylated hydroxytoluene (TBHT), tert-butylated phenol derivative (TBP), tert butyl hydroxquinone (TBHQ) and these antioxidants are proved to be effective on biodiesel and has capacity to extend the Oxidation Stability to 7 Hours respectively [18].

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