Assessment of Oxidation Stability of Oils for Biodiesel Production

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Abstract

As the fossil fuels are depleting day by day, so there is a need to reach for an alternative fuel to meet the energy demand of the world. The various oil sources classified as edible and non edible the edible sources like groundnut, peanut etc are primarily used to meet the food requirement but the excess supplies can be converted to biodiesel. Since India is already importing 70% of the edible oils and therefore the diversion of edible oil for biodiesel production is not possible. The option rests only on the nonedible oils for conversion to biodiesel. The main quality problem with biodiesel is its oxidation stability that plays an important role in determining the quality. Which is the resistance of oil/fats/biodiesel to degradation through oxidation with air. The rapidity of oxidation depends on the degree of unsaturation, the presence of antioxidants, and prior storage conditions. This auto oxidation caused by contact with air during long term storage presents a legitimate concern for oil/biodiesel quality that can be monitoring in term of kinematic viscosity, acid value or peroxide value. This paper focuses on oxidation stability and its effect on non edible oils and their impacts on engine operation.

Keywords - Energy, Oil, Oxidation Stability, Biodiesel, Oxidation stability Index (OSI)

Introduction

India ranks 6th in terms of consumption of energy, which is 3.5% of the total world's commercial energy. The current consumption of diesel in India is about 40MT (40% of the total petroleum product consumption) and was 52MT by during 2013-2014 at a growth rate 6.5% per annum. The domestic production of crude oil and natural gas was around 42.31 MT during 2012-13. Hence there is a huge gap between demand and supply which needs to be met through increased fuel imports or increasing production of biodiesel as substitute of diesel by growing oil seeds, especially, non edible oil plantations without sacrificing the food security of the country (TERI, 2011). Biodiesel is a renewable energy resource that can be obtained by using waste and degraded lands. Biodiesels are the mono-alkyl esters of long chain fatty acids of vegetable oils or animal fats, derived either from plant or animal. Biodiesel requires very little or no modification of engine when blended with diesel up to 20% (B_{20}). Use of bio fuel results in substantial reduction of un-burnt HC by 30%, CO by 20% and particulate matters by 25%. It has no sulphur. Besides, it has nearly 10% in-built oxygen, which facilitates the combustion process and enhances Cetane number (No, S.Y., 2011) (Dwivedi *et al.,* 2014).

Problems of using Oil as Engine Fuel

There are two major problem associated with oil when used in engine i.e. stability and cold flow properties. Both are dependent on fatty acid compositions of oil. i.e. saturated and unsaturated fatty acids present in the oils. Each is briefly discussed as below.

Stability of Oil

The fuel stability is usually in terms of color, soluble gums and insoluble. The color is indicative of sediments. The fuels forming color does not necessarily develop gums and sediments which are predominant stability concerns. The biodiesel and its blends has been found to be more prone to oxidation than the straight vegetable oils (SVO) can develop wide variety of alcohols, aldehydes, peroxide and other insoluble formed during its transport and long term storage and can cause acidity in the fuel and form insoluble gums and sediments increasing operational problems with plugging of fuel filter and fouling and affect the engine operation. In this context, it becomes necessary to study the oxidation, thermal and storage stability of biodiesels and their blends with diesel. The oxidation stability can be used to establish relationship between induction period and other quality parameters. The storage stability studies require the study of the effect of storage conditions like temp., light, atmosphere, presence of natural antioxidants, metals etc on the stability of biodiesel / fuels. Thermal stability is concerned with the effect of temperature on the natural oxidation stability of fuel and the effect of adding natural synthetic antioxidants to stabilize the fuels that can be used over long period of time without any problems. In order to ensure stable biodiesel quality over long period, there is a need to enhance the oxidation, storage & thermal stability of biodiesel & its blends using various natural / synthetic antioxidants under different parameters like light, temp, metals etc .

As stated above fatty acid composition of the biodiesel fuel is an important factor in determining stability towards air. Generally, the polyunsaturated fatty acids (C18:2, linoleic acid; C18:3 linolenic acid) are most susceptible to oxidation (Mejia *et al.,* 2013). Oil /fuel properties can degrade by one or more of the following mechanisms: (i) oxidation or autoxidation from contact with oxygen present in ambient air; (ii) thermal or thermal-oxidative decomposition from excess heat; (iii) hydrolysis from contact with water or moisture in tanks and fuel lines; or (iv) microbial contamination from migration of dust particles or water droplets containing bacteria or fungi into the fuel (Neff *et al.,* 1992). Oxidation stability is distinguished from the term “storage stability” since oxidation may occur not only during storage but also during production and use.

Sarain *et al.,* (2010) stated that the protection of oil quality, which remains suitable to consumers for longer time, is an important objective of quality control in the oil and fat industry. Shelf life of vegetable oils is the main characteristic that influences its suitability and market values. The consequence of lipid oxidation leads to decrease in shelf life and it recognized as the big problem in the food industry. Oxidative stability is one of the most important indications for maintaining the quality of the vegetable oils/biodiesels.

Tan *et al.,* (2002) reported the reaction that essentially consists of an induction stage. The time, before a dramatic increase in the rate of lipid oxidation, is a measure of oxidative stability and is referred to as the induction time. Jain and Sharma *et al.* stated that there are various types of stabilities like oxidation, storage and thermal playing key roles in making the fuel unstable (Agarwal *et al.,* 2013).

Mechanism of Oxidation

The oxidation of fatty acid chain is a complex process proceeded by a variety of mechanisms. The oxidation of biodiesel is due to the unsaturation in fatty acid chain and presence of double bond in the molecule which offers high level of reactivity with O_2, especially, when it is placed in contact with air/ water. The primary oxidation products of double bonds are unstable allylic hydroperoxides which are unstable and easily form a variety of secondary oxidation products. This includes the rearrangement of product of similar molecular weights to give short chain aldehydes, acids compounds and high molecular weight materials The oxidation reactivity is related to the degree of C=C bonds in the fuel. Increased content of the C=C bonds correlates to decreased oxidative stability of the fuel. The increase in instability of a given diesel fuel molecule is generally directly proportional to the number of C=C bonds in the molecule (i.e., a molecule containing two C=C bonds has half the stability of a molecule containing one C=C bond) (Evangelos, 2013; Freire *et al.*, 2012).

Oxidation Stability Index/Oil Stability Index (OSI)

All oils and fats have the resistance to oxidation which depends on the degree of saturation, natural or added antioxidants, or prior use. Oxidation is slow until this resistance is overcome, at which point, the oxidation accelerates and becomes very rapid. The length of time, before this rapid acceleration of oxidation, is the measure of the resistance to oxidation and is commonly referred to as the 'induction period, or Oxidative Stability Index. (Sharma *et al.*, 2010) OSI is defined as the hours required for the rate of conductivity change to reach a predetermined value. This method has been collaboratively studied and accepted by American Oil Chemists Society and determines the relative resistance of oil/fats samples to oxidation and replaces the out dated AOM. These measurements of stability are available, which do take into account double bond position; provide OSI in hours as the oxidation period. This time is known as oxidation/ Induction period. After the induction period, the rate of oxidation increases dramatically (Jain *et al.*, 2010). The BAPE and OSI of SVOs based on the data of table 1 has been calculated using the following equation (Sharma *et al.,* 2010).

BAPE = % C 18:2 + (2× % C 18:3) **(Equation 1)**

OSI = 3.91 (0.045 × BAPE) **(Equation 2)**

Table 1: BAPE and OSI value of various edible and non edible oil (Kumar *et al.,* 2013; Dwivedi *et al.,* 2014).

Oil	% C18:1	% C18:2	% C18:3	BAPE	OSI
Sunflower Oil	17.7	72.9	-	72.9	.62
Soybean Oil	23.2	56.2	4.3	64.8	.99
Cotton seed Oil	13	58	0	58	1.30
Rapeseed Oil	64.1	22.3	8.2	38.7	2.20
Peanut Oil	48	32	1	34	2.38
Seasame Oil	52.8	30.2	-	30.2	2.55
Jatropha Oil	35.8	28.8	0.2	29.2	2.59
Pongamia Oil	51.59	16.64	-	16.64	3.16
Palm Oil	40.5	10.2	0.2	10.6	3.43
Corn Oil	25	6	-	6	3.64
Coconut Oil	5	1	-	1	3.865

The variation of BAPE with OSI for various oil is given in table 1 which shows that oxidation stability of oils is dependent on the amount of fatty acids present in the oil. The BAPE for sunflower oil is max of all the other oils which show of that it is highly unstable while the coconut oil is lowest, which shows that it is highly stable. The variation of BAPE with OSI is given in fig. 1.

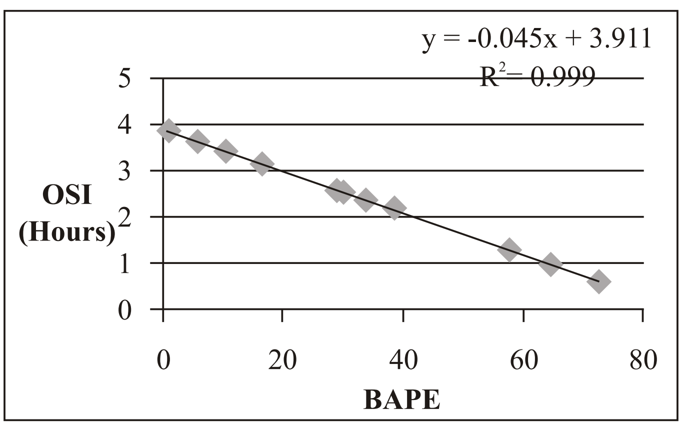

Figure1: OSI vs. BAPE.

The above fig shows the variation of OSI with BAPE for various oil. It shows that as the BAPE increases, the stability of oil decreases.

Problems encountered when Biodiesel and its blends are used as Engine Fuels

Extensive literature survey reveals that most of the engine problems can be attributed to poor quality biodiesel. Some of the problems (primarily cold-weather problems) are not due to poor fuel quality but are related to the biodiesel fuel properties. Most of these problems can be avoided or minimized. Table.2 reviews the possible engine problems while using biodiesel and its blends.

Table: 2 Details the engine problems experienced when biodiesel and its blends with diesel are used an engine fuels and suggest remedial measures (Hancsok *et al*, 2008; Raheman *et al.*, 2004; Dwivedi *et al.,* 2014).

ENGINE PROBLEMS	REMEDIAL MEASURES SUGGESTED
Deposits on injectors affecting the fuel spray patterns.	Injectors may be periodically cleaned. Specialized cleaning equipment is required to clean the injectors precisely.
Cold-weather operation of engine using partially solidified, or by partially transformed biodiesel.	Use of Low-temperature properties improvers to improve the engine operation in cold conditions. To ensure complete conversion of oils to biodiesel free from contaminants.
Engine starting problems cold weather condition or run only a few seconds. Engine stops after operation for few seconds. Possibility of filter clogging due to the presence of gum sediments/particles solidified biodiesel due to poor oxidation stability of the fuel.	Wait for spring time to reach. Warm the fuel filter using 12-volt jacket heaters. Use additives to gum/particle formation in biodiesel.
Fuel filter clogging due to: Poor biodiesel quality due to formation of resins or gels in the fuel supply system. Building up of algae in fuel tank. Deposition of sludge at the bottom of old tanks.	The problem of algae build up can be removed by adding suitable algaecide. Use of moisture free fuel is recommended.
Deposits (gums) in injector pump are indicated by engine starting, misfiring and power losses due to either incomplete biodiesel conversion or partial oxidation of biodiesel.	Proper cleaning of injector pump. Filling the fuel just before it use.
Leakage in fuel supply line.	To ensure that the engine and its parts are compatible with biodiesel utilization.

Conclusion

The performance of straight oil as fuel is dependent on the amount of fatty acids presents in the oil. The variation of fatty acids gives an idea about the oxidation stability. In case of edible oils the OSI is lowest for sunflower oil showing that it is highly unstable while the OSI for coconut oil is maximum which shows that it is highly stable. In case of non edible oils like Pongamia oil have high OSI than Jatropha oil. So Pongamia oil can be used as an alternative to diesel in near future.

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