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Stability of biodiesel – A review

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ABSTRACT

Biodiesel is the common name given to ethyl or methyl esters of long chain fatty acids obtained from vegetable oils or animal fats. Biodiesel is renewable, non toxic, biodegradable and usually contains no sulfur or aromatic compounds. The drawbacks of biodiesel are that it costs more than petroleum based diesel, softens and deteriorates certain elastomers and rubber compounds that are used in parts of fuel injection system such as fuel and pump seals. Another very important problem associated with the biodiesel is its storage as biodiesel is vulnerable to oxidation due to environmental factors such as air, moisture light etc. During oxidation, biodiesel breaks into unwanted smaller chain compounds such as aldehydes, small chain esters etc. beyond tolerable limits. Thus the oxidation process deteriorates fuel quality which can cause problems such as choking of injector and fuel filter and formation of deposits in various components of the fuel system including combustion chamber. Therefore it is essential to conduct the stability analysis of the biodiesel. A lot of work has been published on the stability of biodiesels. This paper discusses in detail about the types, causes and the effects of instability, about various tests and standards used for analyzing stability, various parameters and values used to measure and quantify stability, effects of various external agents such as antioxidants on the Stability. It also discusses the recent trends in the ongoing research in this field. It is the critical study of the previous works done on the stability of the biodiesel.

Contents

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1. Introduction

There is more than one reason to look for alternative to the conventional petroleum fuels. The crude oil reserves are limited and demand for fuels is ever increasing. Not only the transport sector, but also agricultural and industrial sectors are dependent on the fuel supply. This leads to the sharp rise in the prices of crude oil. Since 1999–2000 to 2014–15, the crude oil prices have seen a steep rise from just above 20$/barrel to near 140$/barrel and then back to around 60$ [1]. Therefore when the world is on the verge of facing energy crises as well as environmental crises, researchers all over the world are keenly looking the alternative options so as to reduce this high dependability on conventional fuels. Diesel fuel is mainly used in transportation sector. The demand for diesel in India is 5 times that of the petrol. Therefore it is urgent to find the alternatives for the diesel.

During the last three decades, the vegetable oils have been the focus of the interest of the researchers as the alternative to the conventional fuels. Experiments around the world are being performed on vegetable oils and their derivatives (biodiesels) obtained from various crops like sunflower, soybean, linseed, palm, coconut, rape, peanut, mustard, karanja, jatropha, neem, caster, cotton, etc. The competency of vegetable oils as a CI engine fuel comes from the facts that vegetable oils have good heating value and they give out almost no sulfur or aromatic polycyclic compounds. The two properties of vegetable oils viz. cetane numbers and heating values are comparable to those of the conventional diesel. Also the carbon cycle is completed by their burning as they are derived from plants [2–4].

Though the vegetable oils have the potential of being the substitute of diesel, the use of straight vegetable oils has certain problems associated with them. The viscosity of the vegetable oils is very high (usually 32–40 $mm^2\ s^{-1}$ at 38 °C) as compared to that of the diesel (3–4 $mm^2\ s^{-1}$ at 38 °C). The normal injection as used in diesel engine cannot be used with vegetable oils due to their different atomization characteristics from diesel [5]. Therefore if the straight vegetable oils are to be used as fuels, there is requirement of engine modifications and preheating arrangement [6,7]. Due to this reason, the straight vegetable oils are decomposed by pyrolysis or converted into biodiesel by transesterification reaction [8–13], before using as fuel for diesel engines.

There are many significant advantages of biodiesel over conventional diesel. It is derived from renewable resources, hence leads to less dependency on the conventional fuel. It has higher flash point (150–180 °C) compared to 70 °C of the conventional diesel, leading to safer handling and storage. It has good lubricity, is biodegradable, and causes reduction in exhaust emissions (except NO_x). The drawbacks of using biodiesel as CI engine fuels are its lower energy content leading to lower engine power and speed, higher viscosity, higher pour point, higher cloud point, injector coking, engine compatibility, Higher NO_x emissions, high engine wear and high price [14].

Another problem associated with the biodiesel is that it is sensitive to oxidation when exposed to atmosphere (air, light and moisture etc). During oxidation, the biodiesel breaks into unwanted smaller chain compounds such as aldehydes, small chain esters etc. beyond tolerable limits. In other words, biodiesel becomes chemically unstable. The oxidation process deteriorates fuel quality which can cause problems such as choking of injector and fuel filter and formation of deposits in various components of the fuel system including combustion chamber [15–17]. Therefore it becomes essential to conduct the stability analysis of the biodiesel. A lot of work has been published [1–119] on the stability of biodiesels.

Various factors that affect the stability are air, heat, light, antioxidants, minerals, peroxides, material of the storage container etc. These factors have been investigated in most of the studies. This paper reviews the previous work done by the researchers and summarizes the results of their studies. This paper also enlists various methods and standards that are used to measure the oxidation stability. This work discusses in detail about the types, causes and the effects of instability; various parameters and values used to measure and quantify stability; effects of various external agents such as antioxidants and metal contaminants on the stability of biodiesel.

2. Stability of biodiesel – definition

According to Westbrook [18], “stability of the biodiesel is its ability to resist the physical and chemical changes caused by interaction with the environment”. Biodiesel is susceptible to oxidation, contaminants and interaction with light and temperature. The interactions of fatty acid chains present in the biodiesel with the oxygen makes the fuel unstable. Apart from this, the reactions of alkenes, dienes and compounds containing nitrogen, sulfur and oxygen also play a part in the oxidation phenomenon. Depending upon the amount and type of unstable matter, the effects of the oxidation can be the change in color of biodiesel, deposit formation and other changes which decrease the fuel clarity and cleanliness [18,19].

3. The cause of instability

During the process of transesterification, if the reaction of fatty acid is carried out with methanol, the result is methyl ester of that fatty acid and if it is implemented with ethanol, ethyl ester is formed. During the transesterification process, the fatty acid chain remains unchanged; therefore the oxidation chemistry of biodiesel is similar to that of the fatty acid or oil from which it is derived. It becomes very important to study and understand the chemical composition and structure of the fatty acids and their corresponding methyl or ethyl esters for the proper understanding of the phenomenon of autoxidation.

On the basis of the carbon bonds present, Fatty acids can be classified into two types:

(i) Saturated fatty acids, where no double bonds between two carbon atoms are present
(ii) Unsaturated fatty acids, where carbon-carbon double bonds are present