

Oxidation Stability, Engine Performance and Emissions Investigations of Karanja, Neem and Jatropha Biodiesel and Blends

2011-01-0617

Published
04/12/2011

Deepak Khurana and Avinash Kumar Agarwal
Indian Institute of Technology Kanpur

Copyright © 2011 SAE International

doi:10.4271/2011-01-0617

ABSTRACT

Poor oxidation stability is the central problem associated with the commercial acceptance of the biodiesel. The EU standard (EN14214) specifies a minimum value of 6 h for biodiesel induction period at 110°C, measured with Rancimat instrument. Most of the freshly prepared biodiesel generally have lower induction periods than prescribed by the standards. Anti-oxidants are therefore added to enhance the oxidation/ storage stability of biodiesel. Oxidation is an exothermic process, and the reaction heat evolved makes it possible to use thermo gravimetric analysis (TGA).

In the present study, the oxidation stability of methyl esters derived from Karanja oil and Neem oil, stabilized with anti-oxidant pyrogallol (PY) was studied by DSC. Onset temperature of freshly prepared Karanja biodiesel (KOME) and Neem biodiesel (NOME) was observed to be 148 and 153°C respectively. The stability increases with increasing anti-oxidant dosage. A comparative analysis of oxidation stability of biodiesel/diesel blends was done on biodiesel derived from Karanja (*Pongamia pinnata*), Neem (*Azadirachta indica*) and Jatropha (*Jatropha curcas*) oil using Rancimat instrument. Jatropha biodiesel (JOME)/ diesel blends were observed to be most stable compared to KOME and NOME/ diesel blends. Further in this study, emissions and performance tests were conducted on an IDI diesel engine for diesel, B100, and biodiesel dosed with 1000 ppm of PY to experimentally evaluate adverse effects of anti-oxidants on biodiesel performance and emissions. With anti-oxidants dosed biodiesel, THC and CO were found to be slightly higher compared to diesel and B100. However the difference was not significant. Thermal efficiency and BSFC

of anti-oxidants dosed biodiesel was comparable to diesel and B100.

INTRODUCTION

Vegetable oils and their esters (Biodiesel) are the promising alternative fuels for diesel engine. The biodiesel feedstock varies from country to country depending on the availability of vegetable oil in the vicinity and the Government policies. Traditional raw materials for biodiesel production in the west are Soybean oil, Rapeseed oil, Sunflower oil, Palm oil, Rice-bran oil etc. Since India is a net importer of edible oils, these cannot be used for production of biodiesel. Still, India has the potential to be a leading global producer of biodiesel, as biodiesel can be produced from non-edible oils like Jatropha, Karanja, Neem, Mahua, Castor, Linseed, Kusum etc. Many of these oils are not being utilized fully. Out of these feedstocks, India is focusing on Jatropha and Karanja, which can grow in arid zones and wastelands of the country. India has about 80-100 million hectares of wasteland, which can be used for the cultivation of Jatropha and Karanja. India is also one of the largest producers of Neem oil, which is an untapped resource in India. Oxidation of these esters in presence of air, high temperature and metal exposure is a major hindrance for its commercialization. The ill effects of oxidation of biodiesel are increased viscosity, peroxide value, acid number, and gum deposits. An increase in these properties of biodiesel cause problems in the engine like damage to fuel delivery system, filter plugging, injector coking, corrosion, hardening of rubber components, fusion of moving components and engine deposits etc. Therefore the main objective of this study is to investigate the oxidation stability, engine performance and emissions of biodiesel derived from non-edible oils of sub-continental origin such as Karanja, Neem and Jatropha.



Documents

Document Sharing Hub

The European Committee of Standardization (CEN) in its standard EN14214 has specified a minimum of 6 h induction period at 110°C for biodiesel, measured with Rancimat instrument [1, 2]. The heat content of vegetable oils and their esters is nearly 90% that of diesel fuel [3, 4, 5]. The stability of biodiesel is classified as oxidation stability, thermal stability and storage stability. However all these are broadly termed as oxidation stability. Thermal instability is related to the increased rate of oxidation at higher temperature which in turn increases the weight of the molecules due to the formation of insolubles. In an engine, extra fuel from the injector returns back to the fuel tank. Being in contact with hot fuel injector installed in the cylinder head, the fuel gets exposed to heat for a considerable duration. This could be a problem in case of biofuels, such as biodiesel, which start changing their properties, once they are exposed to heat. Biodiesel should therefore be able to retain its thermal stability at higher temperatures. There is no thermal stability limit specified for biodiesel in any standard prescribed internationally. However from a practical stand point, a biodiesel sample, which maintains its thermal stability up to 150°C can be regarded as thermally stable. Differential Scanning Calorimetry (DSC) is an accelerated method, which finds the temperature at which the oxidation reaction takes place. This temperature is termed as oxidation onset temperature [6].

The oxidation stability of biodiesel can be improved with addition of anti-oxidant additives. All the anti-oxidants have an aromatic ring with at least one hydroxyl (–OH) group. The hydroxyl (–OH) group of the anti-oxidant is very active so that hydrogen is abstracted from –OH and donated to the oxidized free radical to inhibit the rate of oxidation (Figure 1). The resulting anti-oxidant is a stable radical that can react with other fatty acid free radicals and further contribute to oxidation inhibition [7-8].

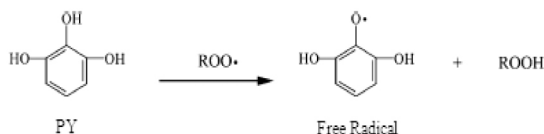


Figure 1. Mechanism of anti-oxidant activity.

LITERATURE REVIEW

Operating diesel engine produces hazardous emissions which may affect the environment and adversely affect the human health [9, 10, 11] e.g. Oxides of Nitrogen (NO_x) irritate the eyes and throat, and create breathing problems; Carbon monoxide (CO) reduces the oxygen carrying capacity of the blood; Sulfur dioxide (SO₂) reduces the lung resistance causing chronic bronchitis and also acid rain; Poly-cyclic aromatic hydrocarbons (PAH) can cause cancer; Carbon dioxide (CO₂) leads to global warming; and Particulate

Matter (PM) results in respiratory diseases like asthma and emissions of hydrocarbon (HC) results in loss of fuel. Biodiesel is however a clean burning fuel with little or no SO₂, lower THC, CO, PM and CO₂ emissions with possibly slightly higher NO_x. But for practical feasibility of biodiesel, anti-oxidants are added to increase the storage stability of biodiesel. This study is aimed at experimental assessment whether these additives affect the emission characteristics of biodiesel significantly.

Sharma et al. [12] used DSC method for determining the oxidation stability of lubricating oil with reasonable accuracy and repeatability. Perez et al. [13] used DSC method to understand the oxidation stability and cold flow properties of various blends with mineral diesel. Robert O Dunn [14] investigated the effectiveness of five anti-oxidants on the oxidation stability of Soybean oil methyl esters (SME). Anti-oxidant examined were 2-tert butyl hydroquinone (TBHQ), 6-di-tert butyl-4-methyl phenol (BHT), 2-tert butyl-4-methoxy phenol (BHA), 3,4,5-tri hydroxy benzoic acid (PG) and α -Tocopherol (α -T). The anti-oxidants activity was determined in terms of increasing oxidation onset temperature by using a non-isothermal pressure differential scanning calorimeter (P-DSC). Increasing anti-oxidant loading showed a sharp increase in stability up to 1000 ppm followed by smaller increase in stability at higher concentrations. As such, there is no specification limit for onset temperature for thermal oxidation stability measured by DSC. Though a stability of 150°C in dynamic mode and 160°C in static mode showed a quite stable biodiesel. PG and BHA showed higher thermal stability in static mode at all concentrations followed by TBHQ, BHT and α -T respectively. Whereas in dynamic mode, PG and BHT showed higher oxidation onset temperature followed by BHA, TBHQ and α -T respectively. An anti-oxidant loading of 2000 ppm showed an onset temperature of nearly 150°C for anti-oxidants except α -T in dynamic mode and nearly 160°C in static mode. The onset temperature at 2000 ppm of α -T was 146°C in static and 128°C in dynamic mode. Effectiveness of anti-oxidants in static mode was in the order BHA~PG>TBHQ>BHT> α -T and in dynamic mode the order was BHT~PG>BHA>TBHQ> α -T.

Polvaka et al. [15] studied the effect of 1,2,3 tri-hydroxy benzene (PY) and BHT on the oxidation stability of biodiesel derived from Rapeseed oil and Waste frying oil using Rancimat method as well as differential scanning calorimeter (DSC). Both distilled and undistilled samples of Rapeseed oil and waste frying oil were analyzed. The effectiveness of BHT and PY was analyzed in the concentration range of 0-1000 ppm. It was observed that the oxidation onset temperature increases with an increase in concentration of the anti-oxidant. The onset temperature for untreated distilled waste frying oil was 185°C. The onset temperature with PY was higher than BHT at all concentrations. At 500 ppm

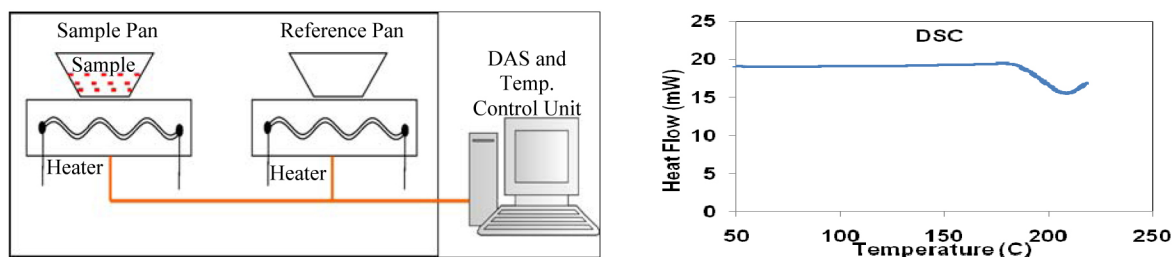


Figure 2. Principle of Differential Scanning Calorimetry (DSC).

concentration the onset temperature was 189°C and 197°C for BHT and PY respectively, while at 1000 ppm, values were 191°C and 198°C for BHT and PY respectively. Analysis was also done on the effects of ramp rate on the onset temperature of Rapeseed oil biodiesel. With the increasing ramp rate from 1°C/min to 15°C/min, the onset temperature increases. Again PY and BHT showed higher onset temperature than untreated Rapeseed oil. In the same study, the effectiveness of anti-oxidants on the induction period was also evaluated using Rancimat method. A constant concentration of 400 ppm of PY and 500 ppm of BHT was analyzed with Rapeseed oil methyl esters and Waste frying oil methyl esters- both distilled and undistilled. The induction periods of distilled samples were lower than corresponding undistilled samples. None of the untreated distilled samples had the stability limit of 6 h while neat distilled samples were having stability more than 6 h. Maximum stability (25.3 h) was observed for undistilled Rapeseed oil methyl ester with 400 ppm of PY anti-oxidant. Samples treated with BHT also obtained the EN 14214 limit except with distilled Waste frying oil methyl ester samples (5.35 h).

Experiments have been done to find the exhaust emissions of biodiesel dosed with anti-oxidants [16]. It was observed in these studies that there was no noticeable increase in PM, THC, CO and CO₂ emissions compared to pure biodiesel. Surprisingly NO_x emissions were reported to have reduced by using anti-oxidant dosed biodiesel [16]. It was inferred that the anti-oxidants which are responsible for stabilizing the biodiesel for longer time, when applied to practical conditions, have no noticeable negative effect of exhaust emissions.

MATERIALS AND METHODS

For the present study, Karanja, Neem and Jatropha oils were procured. Karanja oil methyl ester (KOME), Neem oil methyl ester (NOME) and Jatropha oil methyl ester (JOME) were produced using transesterification process. High grade methanol (6:1 molar ratio) mixed with alkali (NaOH) catalyst (1% w/w_{oil}) was added to the reactor containing pre-heated vegetable oil. The transesterification reaction was carried out at 55-60°C at a stirring speed of 700-800 rpm for 1 hour. After completion of the reaction, reaction products were

transferred to a separating funnel, where upper phase (biodiesel) was separated from lower phase (glycerol) followed by subsequent washing (by distilled water) and drying of the final product i.e. biodiesel.

NOME was produced by a two-step process due to very high free fatty acid (FFA) content of the Neem oil. With feedstock containing high FFA, conventional biodiesel production by base catalyzed transesterification process is not suitable. A two-step process is used. It includes pre-treatment of the high FFA vegetable oil with sulfuric acid i.e. esterification process proceeded by conventional transesterification process. In the first step, esterification is done to reduce the FFA content of the Neem oil by converting FFA into esters. The second step is transesterification process as described earlier, in which triglyceride portion of the oil reacts with methanol in presence of NaOH to form esters and glycerol [17-18].

Thermal stability of biodiesel can be measured by DSC instrument. DSC is a thermo-analytical technique, in which, the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment (Figure 2). Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time.

The basic principle underlying this technique is that, when a sample undergoes a physical transition such as phase transformation or oxidation, relatively higher or lower heat flow will be required compared to the reference in order to maintain both at the same temperature. Whether higher or lower heat must flow to the sample depends on whether the process is exothermic or endothermic. Since the oxidation reaction for biodiesel is exothermic, therefore DSC can be used to study the oxidation stability of biodiesel. A differential scanning calorimetry instrument (Model: DSC-6; Make: Perkin Elmer) was used for measuring the oxidation stability of biodiesel samples. Fuel samples of 10±0.5 mg were weighed into open aluminum pans and placed in the sample chamber of the equipment. Temperature was programmed from 30 to 300°C at the ramp rate of 10°C/min. Purified oxygen (99.8%) was passed through the sample enclosure as a purge gas at a flow rate of 60 ml/min.