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Experimental investigations of oxidation stability of biodiesel produced from *Prunus armeniaca oil* (apricot oil) and effect of various antioxidants on stability, engine performance and emissions

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ABSTRACT

In this experimental investigation, the effectiveness of five different antioxidants: 2-tert butyl hydroquinone (TBHQ), 2,6-di-tert butyl-4-methyl phenol (Butylated Hydroxy Toluene or BHT), 1,2,3 tri-hydroxy benzene (Pyrogallol or PY) and 3,4,5-tri hydroxy benzoic acid (Propyl Gallate or PG), 2-tert butyl -4-methoxy phenol (Butylated Hydroxy Anisole or BHA) on oxidation stability of biodiesel produced from the Prunus armeniaca oil (apricot oil) on the bases of weight of sludge and neutralization value has been studied. The quantities of antioxidants 100, 1000, 4000 ppm were added in the sample and the oxidation stability was measured using Rancimat apparatus. Among all aforementioed antioxidant, PG and BHA gives best result at room temperature as well as 110 °C.

In this study, engine emissions and performance were tested on a Kirloskar TV1, single cylinder engine to analyze the effect of BHA and PG antioxidants. Engine emissions and performance were experimentally found for, 20% biodiesel blend in 80% diesel (B_{20}), B_{20} with 4000 ppm concentration of antioxidant PG (B_{20}/PG4000), B_{20} with 4000 ppm concentration of antioxidant BHA (B_{20}/BHA4000) and diesel are plotted against load.

It was found from experiments that CO emissions from B_{20}/BHA4000 fuel are lower than diesel at full load while that of B_{20}/PG4000 blend, CO emission was similar as diesel at full load. HC emission was found minimum for B_{20}/BHA4000 among all four blends at full load. At low load NOx emission in B_{20} was lower and it increases with increase in engine load. NOx emission with B_{20}/BHA4000 and B_{20}/PG/4000 blend at full load was found to be minimum as compared to diesel.

1. Introduction

Biodiesel refers to vegetable oils or animal fat-based fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting lipids (triglyceride) with an alcohol produce fatty acid esters in the presence of a catalyst. The catalysts commonly used are NaOH and KOH [1]. The fatty acid alkyl esters obtained after the transesterification reaction are commonly referred as biodiesel. Biodiesel has great potential as an alternative fuel for C.I. engines. Biodiesel has a lot of advantages such as high cetane no. [2,3], biodegradable, non-toxic, renewable, contain molecular oxygen which helps in the combustion of fuel, have potential to significantly reduce harmful emissions and have no sulphur content [4,5]. However, the biodiesel shows a remarkable challenge because of high-cost feedstock and increasingly aggravating tension between energy crisis and food security [6]. In this dilemma, the production of biodiesel from the cheaper feedstock, such as high free fatty acid (FFA) non-edible oil could be an economical way to meet the current cost issues involved in the production. On the other hand, India is the world's 3rd largest consumer of crude oil and petroleum products after United state and China [7]. India imports about eighty-six percent of crude from the Organization of the Petroleum Exporting Countries (OPEC). The India imported 3.86 million barrels of crude oil last year [8]. Hence it become inevitable to search renewable (non-conventional) feed stocks for biodiesel production. Some recent studies of biodiesel from non- conventional feedstock's include Mahua, Milo, Moringa, Oleifera, *Prunus dulcis*, *Prunus armeniaca*, *Croton megalocarpus*, *Camelina*, and others [9–15].

Wild Apricot (*Prunus armeniaca L.*) belongs to the Rosaceae family of the Rosales group. It is an important fruit tree species found in temperate regions of Jammu and Kashmir's Ladakh region grows most of the India Apricots. The seed kernel oil of apricot can be used for edible oils, lubricants, cosmetics and in the prevention of cardiovascular diseases [16]. Biodiesel have almost all fuel properties similar to diesel however, biodiesel still have many disadvantages one of them is

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oxidation stability. One way to improve the resistance of biodiesel to auto-oxidation is by adding an antioxidant, while another is to mix them with diesel fuels. Although biodiesel oxidation is difficult to avoid but can be appreciably slowed by the use of antioxidants. Sendzikiene et al. [17] studied the oxidation stability of four types of biodiesel using the rancimat apparatus. The oxidation stability of two vegetable oils based biodiesel samples namely rapeseed oil methyl ester (RME) and linseed oil methyl ester (LME) were higher than two animal based biodiesel namely lard methyl ester (PME) and Tallow oil methyl ester (TME). Sarin et al. [18] have studied the influence of metal contaminants on the oxidation stability of Jatropha- based biodiesel in the presence of transition metals (iron, nickel, manganese, and cobalt) was found to depress the oxidation stability of biodiesel, as measured by the induction period. The effect of metals on the stability of biodiesel is catalytic because the induction period of biodiesel becomes constant at some higher concentration and above for all metals. Copper shows the strongest catalytic effect for oxidation, and all other metals also showed catalytic effects on biodiesel oxidation. Yang Z. et al. [19] studied the factors affecting oxidation stability for several commercially available biodiesels were primarily investigated by acid value (AV) and induction period (IP) evaluations in this study. It was found that the measured IP at different storage time/different storage atmosphere were somewhat dependent on the saturated degree of fatty acid methyl esters (FAMEs). AV increased and IP decreased after one year of storing in a dark cold room in an air-tight tank, Solvents (methanol, acetone and water) did not show a contribution to altering IP but metals (copper and lead) showed the strongest detrimental effects to oxidative stability. The presence of PY or TBHQ showed the strongest enhancement of induction periods. Copper and lead showed a strong catalytic effect on decreasing oxidative stability, but not for steel and aluminum alloy. Aluyor et al. [20] studied antioxidant activity involves the donation of hydrogen of free radical followed by the formation of complex bond between a lipid radical and the antioxidant radical formed as a result of hydrogen loss. The scheme of antioxidant activity is shown in Fig. 1. Studies on the antioxidant effect on biodiesel reveal that for most of the biodiesel types, PY and PG are found most effective, while some studies showed that effectiveness of antioxidant depends upon type of oil and quantity of antioxidant used. But these synthetic antioxidants are more effective than natural antioxidants like α-Tocopherol (α-T) or vitamin E [21–22]. The chemical structure of some of the antioxidants is given in Fig. 2. Domingos et al. [23] studied the effect of commercially available antioxidants (BHA, BHT and TBHQ) on the oxidation stability of soybean oil ethyl esters using rancimat apparatus the antioxidants were dosed with 0 to 8000 ppm concentration. It was inferred that if the initial stability is very low, a high concentration of antioxidant are required to meet the EN-14214 specifications. Tang H. et al. [24] studied the effectiveness of various natural and synthetic (antioxidants) i.e. PG, PY, TBHQ, BHT, BHA, DTBHQ, and ionol BF200 (IB) to improve the oxidative stability of soybean oil (SBO-), cottonseed oil (CSO-), poultry fat (PF-), and yellow grease (YG-) based biodiesel at the varying concentrations between 250 and 1000 ppm. It indicated that natural antioxidants play a significant role in determining oxidative stability. Moreover PG, PY, TBHQ, BHT, BHA, and IB can enhance the oxidative stability of these different types of biodiesel. Ryu K. [25] studied the effect of five antioxidants i.e. Butylated Hydroxytoluene (BHT), Butylated Hydroxyanisole (BHA), Tert-Butyl Hydroquinone (TBHQ), Propyl Gallate (PG) and α-Tocopherol. From the experimental investigation, it is clear that TBHQ, BHA, and BHT were the most effective and α-tocopherol was the least effective in increasing the oxidation stability of biodiesel. Leung D.Y.C. et al. [26] investigated the degradation characteristics under different storage conditions of rapeseed oil based biodiesel. Two types of test were conducted to determine the rate of degradation: the purity test and the acid value test. It was found that the samples stored at a temperature below 20 °C, purities (tested on gas chromatography) temperature decreased from 99.7% to 92.5% after 52 weeks. Das L.M. et al. [27] examined, "long-term storage stability of Karanja oil methyl ester (KOME). KOME was prepared and stored for a period of 180 days under different storage conditions. The oxidative stability of KOME decreased i.e. the peroxide value and viscosity increased with increase in storage time of the biodiesel. It was found that propyl gallate is the best antioxidant for KOME followed by BHA and BHT.

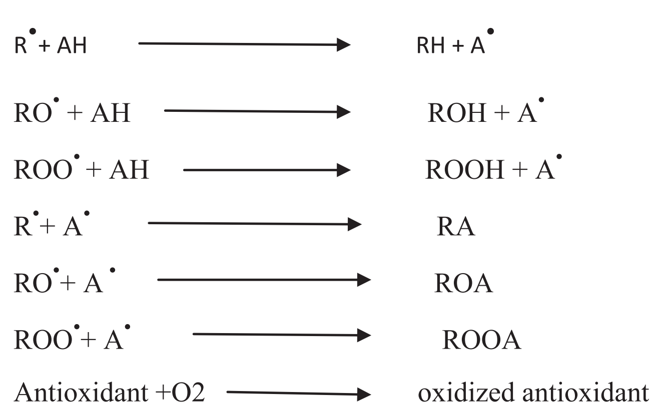

Fig. 1. Antioxidant activity, showing donation of hydrogen to free radical.

There are many studies available on the performance and emission analysis of biodiesel [28–32]. The antioxidant showed little (either increase or decrease) influence on the engine performance and fuel properties. Ryu K. [33] studied the effect of antioxidants on the oxidation stability, performance and exhaust emissions from a diesel engine fueled with Soybean based biodiesel. Biodiesel was dosed with antioxidants TBHQ and PG in the concentration of 0, 300, 500, 1000 and 2000 ppm and the results of exhaust emissions were compared with diesel. At lower loads, the HC, NOx, and smoke were comparable with diesel while at higher loads; HC and smoke were very high with diesel fuel compared to biodiesel with or without antioxidants. NOx emissions with diesel were lower than biodiesel with or without antioxidants. No appreciable difference was observed in NOx emission with neat biodiesel and biodiesel dosed with antioxidants. With both the antioxidants (TBHQ and PG), no difference in HC, smoke and NOx was observed between fuel with or without antioxidants. It was inferred that the antioxidants which are responsible for stabilizing the biodiesel for a longer time, when applied to practical conditions, have no noticeable negative effect of exhaust emissions. In the same study, the antioxidant TBHQ was dosed in the concentration ranging from 300 to 2000 ppm to perform the performance test on the diesel engine. Gan Suyin et al. [34] studied the effect of antioxidant (BHA, BHT and TBHQ) addition in palm oil methyl ester blend with diesel on emission. It was found that both BHA and TBHQ were effective in lowering NO_X and B_{20}/B_{10}/BHA blend was effective in lowering CO as compared to other blend.

From literature survey, it is concluded that the biodiesel fuel properties can deteriorate during storage. The presence of the metals was found to depress the oxidation stability of biodiesel due to the acceleration of free radical oxidation. Copper had a strongest catalytic effect. Induction period increased with the increasing concentration of antioxidants. Antioxidants: TBHQ, PG, and BHA decrease NOx emission compared to untreated B_{20}. Antioxidants have no noticeable negative effect on exhaust emissions as well as performance characteristics of CI engine.

This study investigates the oxidation stability of biodiesel made from *Prunus armeniaca* oil (apricot oil) using Rancimat apparatus. The effects of antioxidants in biodiesel on stability, engine performance, and exhaust emission are also studied.

2. Materials and method

There are several factors to be kept in mind while oil selection such as availability of oil, quality of feedstock, energy content, fatty acid