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Study of antioxidant effect on oxidation stability and emissions in a methyl ester of neem oil fuelled DI diesel engine

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ABSTRACT

Biodiesel as an alternative diesel fuel prepared from vegetable oils or animal fats has attracted more and more attention because of its renewable and environmental-friendly nature. But biodiesel undergoes oxidation and degenerate more quickly than mineral diesel. Further several studies report NO_x emissions increases for biodiesel fuel compared with conventional diesel fuel. In this paper, the experimental investigation of the effect of antioxidant additive (Butylated hydroxytoluene) on oxidation stability and NO_x emissions in a methyl ester of neem oil fuelled direct injection diesel engine has been reported. The antioxidant additive is mixed in various proportions (100–400 ppm) with methyl ester of neem oil. The oxidation stability was tested in Rancimat apparatus and emissions, performance in a computerized 4-stroke water-cooled single cylinder diesel engine of 3.5 kW rated power. Results show that the antioxidant additive is effective in increasing the oxidation stability and in controlling the NO_x emissions of methyl ester of neem oil fuelled diesel engines.

1. Introduction

Biodiesel is one of the substitutes to fossil diesel fuel today in the world. Biodiesel production and demand have been growing fast and will continue to do so [1]. The biodiesel usage doesn't increase global warming as it happens in fossil fuels. As the vegetable oil plants in nature absorb carbon dioxide thereby compensate CO_2 emissions, which are emitted during its usage as biodiesel fuel [2]. While growing, the plants absorb carbondioxide. When burnt, biodiesel emits the same amount of CO_2 as the plants absorb in growth and hence no greenhouse effect and global warming [3].

But biodiesel undergoes oxidative degradation over time due to the significant amount of fatty acids with double bonds present in it. Storage stability of a fuel is its ability to resist physical and chemical changes brought about by its action with the environment. The problems arising from the deterioration of the fuel properties of biodiesel during storage are expected to be more severe than diesel fuel. The oxidation can result in the formation of corrosive short-chained acids and deposits that may cause increased wearing of engine fuel pumps. The storage problems can be caused by the chemical composition of biodiesel and the storage conditions. Fatty acid methyl esters are the main chemical composition for biodiesel and will vary with feedstocks by chain lengths and levels of unsaturation [4]. Contact with ambient air, exposure to sunlight, metals, and exposure to high temperature conditions accelerate the oxidation reactions leading to lower oxidation stability of biodiesel. The European Union (EU) biodiesel standard (EN14214) specifies a minimum value of 6 h for biodiesel induction period at 110 °C, measured using Rancimat instrument [5]. In order to ensure the oxidation stability specification limit 6 h for biodiesel at the filling station, the initial oxidation stability at the time of production should be definitely higher than 6 h [6]. Addition of synthetic antioxidants is an efficient way to increase the initial oxidation stability of biodiesel.

Except NO_x, emissions like unburned hydrocarbon, carbon monoxide, particulate matter, sulphates, polyciclic aromatic hydrocarbons, nitrated polyciclic aromatic hydrocarbons and ozone potential of speciated HC are less. For 100% biodiesel, NO_x emission increases by 13% more than that for petrodiesel [7]. NO_x is a major cause of smog, ground level ozone and also a cause of acid rain. As the use of biodiesel has

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increased tremendously, the rise in NO_x emission can become a significant barrier to market expansion. The development of improved NO_x reduction technologies is therefore critical to the global environment [8].

NO_x is generated during combustion by three mechanisms: thermal, prompt, and fuel. High combustion temperature (1700 K) breaks the strong triple bond of nitrogen molecules and form highly reactive atomic nitrogen, which reacts with oxygen and generates thermal NO_x. According to prompt mechanism, formation of free radicals in the flame front of hydrocarbon flames leads to rapid production of NO_x. The fuel NO_x is formed by the reaction of nitrogen bound in the fuel with oxygen during combustion [9].

Thermal and prompt NO_x are the dominant mechanisms in biodiesel-fuelled engines since biodiesel does not contain fuel bound nitrogen. Thermal mechanism is largely unaffected by fuel chemistry, where as prompt mechanism is sensitive to free radical concentrations within the reaction zone. The free radicals formation during combustion determines the rate of reaction and prompt NO_x production. Free radical is a highly reactive molecule with one or more unpaired electrons. Examples include oxygen molecule, nitric oxide, superoxide ion and hydroxyl radical. Antioxidant delays or inhibits oxidative processes by donating an electron or hydrogen atom to a radical derivative.

In this study, methyl ester of neem oil (MENO) is used as a test fuel and Butylated hydroxytoluene as antioxidant. This paper, presents the outcome of investigation on the effect of antioxidant on oxidation stability and emissions of a neem derived biodiesel fuelled direct injection diesel engine.

2. Experimentation

2.1. Test fuels

Neem oil is light to dark brown in colour, bitter in taste and has a strong odour. Neem oil can be obtained from solvent extraction of the neem seed, fruit, oilcake or kernel. A large industry in India extracts the oil remaining in the seed cake using hexane [10]. The neem tree is native to India [11] and Burma and almost the whole tree is usable for various purposes such as medicines, pesticides and organic fertilizer. Neem can be grown on very marginal soils that may be very rocky, shallow, dry, or pan forming. Neem tree can tolerate some extreme conditions like temperature of 45 °C and rainfall less than 35 cm per year [12]. Neem tree get full maturity in just 10 years and gives an average seed yield of around 5.25 tonnes per hectare and has oil content of 45%. As the energy ratio of neem biodiesel is around 1.64, it is considered as one of the best renewable fuels in view of environmental impacts. Azadirachtin is the main constituent of neem seed oil, which varies from 300 to 2500 ppm depending on the extraction technology and quality of the neem seeds crushed [13]. The oil contains sulfurous compounds, which gives it a pungent odour and a less clean burn than other vegetable oils. It comprises of Triglyceride and Triterpenoid compounds.

2.2. Transesterification

Initially the neem oil and methyl alcohol is mixed in 6:1 molar proportion and heated to about 55 °C and then this combination is mixed with 2% NaOH and maintained at 60 °C for 60 min. Then it is allowed to settle by gravity for 24 h [14]. Thus the methyl ester of neem oil termed as biodiesel is produced. The esterified neem oil contains a little amount of water, which is removed by heating the oil before using in the engine [15]. The higher percentage of esters alkanes and absence of phosphorous and sulphur make this esterified neem oil, the future candidate for alternative environment friendly diesel fuel. The measured properties of diesel fuel, neem oil and methyl ester of neem oil are given in Table 1.

Chemical structure and specifications of Butylated hydroxytoluene are given in Table 2. Butylated hydroxytoluene is accurately weighed using a high precision electronic weighing balance and added to measured quantity of neem biodiesel. To make 0.010%-m of antioxidant mixture 100 mg of antioxidant is added to 1 kg of biodiesel. The oxidation stability and emissions from the engines were studied at different biodiesel and antioxidant mixtures 0.010%-m (MENO + BHT100), 0.020 %-m (MENO + BHT200), 0.030 %-m (MENO + BHT300), 0.040 %-m (MENO + BHT400), with a mean engine speed of 1500 rpm. A 3000-rpm speed mixer is used to prepare a homogeneous mixture of antioxidant and fuel.

2.3. Experimental setup

Oxidation stability of biodiesel samples with varying dosage of antioxidants was studied using Rancimat instrument. This is a computer controlled measurement instrument for determining the oxidation stability of biodiesel according to EN 14112, which is included in the EU biodiesel standard EN 14214. The main parts of Rancimat include reaction vessel, measuring vessel and electrode for measuring conductivity. Biodiesel samples are kept at a constant temperature of 110 °C and air at a flow rate of 10 l/h bubbles through each sample. Each measuring vessel contains distilled water (60 ml). The products of biodiesel oxidation are transferred into measuring vessel with the air bubbling through the distilled water. The conductivity of distilled water is continuously monitored by the electrodes. The oxidation of biodiesel is recognized by the sharp increase in conductivity of water due to absorption of oxidized organic acids (formed due to oxidation of biodiesel) into the distilled water.

Table 1
Comparisons of important properties of test fuels.

Properties	Standard Method	Diesel	Neem Oil (NO)	Methyl Ester of NO (MENO)
Density (g/cm^3)	ASTM D941	0.8359	0.944	0.890
Net calorific value (kJ/kg)	ASTM D240	44500	39742	40678
Kinematic viscosity (Cst)	ASTM D613	2–3	38.2	4.27
Flash point (°C)	ASTM D445	75	201	180
Cetane number	ASTM D93	51	55	53