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Study of the oxidation stability and exhaust emission analysis of *Moringa olifera* biodiesel in a multi-cylinder diesel engine with aromatic amine antioxidants

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In this study, the two most effective aromatic amine antioxidants N,N′-diphenyl-1,4-phenylenediamine (DPPD) and N-phenyl-1,4-phenylenediamine (NPPD), were used at a concentration of 2000 ppm. The impact of antioxidants on the oxidation stability, exhaust emission and engine performance of a multi-cylinder diesel engine fuelled with MB20 (20% Moringa oil methyl ester and 80% diesel fuel blend) were analysed at varying speed conditions at an interval of 500 rpm and a constant load. It was observed that, blending with diesel enhanced the oxidation stability of the moringa biodiesel by approximately 6.97 h, and the addition of DPPD and NPPD to MB20 increased the oxidation stability up to 34.5 and 18.4 h, respectively. The results also showed that the DPPD- and NPPD-treated blends reduced the NOx emission by 7.4% and 3.04%, respectively, compared to the untreated blend. However, they do have higher carbon monoxide (CO) and hydrocarbon (HC) levels and smoke opacities, but it should be noted that these emissions are still well below the diesel fuel emission level. The results show that the addition of antioxidant with MB20 also improves the engine's performance characteristics. Based on this study, MB20 blends with amine antioxidants can be used in diesel engines without any modification.

1. Introduction

The production of biodiesel from edible vegetable oil sources, which are examples of potential feedstocks, can meet the energy demand and emission regulations [1–5]. There are two sources for the production of biodiesel, edible and non-edible oil sources. The most widely recognized biodiesel sources from edible oils are palm oil, rapeseed oil, sunflower oil, coconut oil, and shelled nut oil, and sources from non-palatable oil include Jatropha curcas, neem, cotton, jojoba, elastic, Moringa oleifera, Mahua, and castor [6–10]. Biodiesels are mostly produced using homogeneous catalysts such as NaOH and KOH. However, because of some limitations, recently, heterogeneous catalysts are used for permitting continuous biodiesel production from different feedstocks [11]. Biodiesel derived from various sources have different properties because of their basic elements, such as the chain length, branching, number, position and the geometric configuration of the double bonds.

Currently, the oxidation stability of biodiesel is of major concern because of the application of biodiesel in the transport and industry sectors. Biodiesels still have various downsides related to their long-term thermal stability and low-temperature flow properties. Specifically, it is difficult to maintain their quality because of their low cold filter plugging point during long-term storage. Atmospheric air causes the autoxidation of biodiesel in storage, which can reduce the fuel quality by adversely influencing its properties, for example, the kinematic viscosity and acid value. Biodiesel oxidation is not just influenced by the presence of air and light but also by a variety of factors, including the composition of the fuel itself and the conditions of storage [12]. The storage stability and inferior oxidative are the significant disadvantages of biodiesel fuel [13,14]. It is well recorded that biodiesel mainly degrades because

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Nomenclature:

ASTM	American society for testing and materials
AOs	Antioxidants
BP	Brake power
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
BHT	2,6-di-tert-butyl-4-methylphenol
BHA	2(3)-tert-Butyl-4-methoxyphenol
CMOO	Crude *Moringa oleifera* oil
CAS No	chemical abstracts service registry number
CO	Carbon monoxide
DPPD	N, N′-diphenyl-1, 4-phenylenediamine
FAC	Fatty acid composition
HC	Hydrocarbon
mm	millimetre
MJ/kg	Mega joule/kg
MOME	*Moringa oleifera* methyl ester
MB	Moringa biodiesel
MBEBP	2,2′-methylenebis(4-methyl-6-tert-butyphenol)
MCD	Multi-cylinder diesel engine
NO_x	Oxides of nitrogen
NPPD	N-phenyl-1,4-phenylenediamine
PM	Particulate matter
rpm	Revolution per minute
TBHQ	tert-butylhydroquinone

of its autoxidation in the presence of atmospheric oxygen [15,16]. Biodiesels are more prone to degradation compared to fossil diesel because of fatty acid chain unsaturation. If two or more bonds of carbon-like (double) poly-unsaturations are present in the fatty chain, then the degradation of the biodiesel is exasperated [17,18]. Treating biodiesel with AO is a useful solution for increasing the resistance of biodiesel against autoxidation without significant modification of the fuel properties [19]. The stabilization factor is F=IPx/IPo, where IPx = induction period in the presence of the antioxidant and IPo = induction period in its absence, and is used to identify the effectiveness of an AO. Peroxyl radicals (ROO°) are isolate radicals in the antioxidant in the group of −OH [20]. The oxidation reaction rate is decided by the free radical. The most vital reactive radicals formed at the time of the combustion reactions are the hydroperoxyl (•OOH), hydroxyl (HO•), alkoxyl (RO•) and peroxyl (ROO•) radicals. These radicals react with N2 and N2O to form nitrogen oxides. Free radicals from the ester can be formed by the four following ways: the bimolecular reaction with hydrogen molecule abstraction by dioxygen from the weakest CH bond, the bimolecular expansion of dioxygen to the double bond of unsaturated ester, the trimolecular reaction of dioxygen with the weakest CH bonds of two unsaturated esters and the trimolecular reaction of dioxygen with the double bonds of two molecules of unsaturated esters [21].

Antioxidants significantly slow down the biodiesel degradation process. The addition of a small amount of antioxidants into the fuel inhibits the formation of the free radical by reacting with peroxyl radicals to form new inert radicals, thus obstructing the propagation step. The hydrogen giving capacity of a chain breaking antioxidant has an essential impact on its antioxidant activity. The hydrogen is discharged from the weak OH (phenols and hydroquinones) and NH (aromatic amines and diamines) bonds of the antioxidants. As indicated by their mode of action, antioxidants are classified as free radical eliminators, metal ion chelators equipped for catalysing lipid oxidation, or oxygen scavengers that react with oxygen in a closed system [16,22]. These are primary AOs, which react with high-energy lipid radicals to convert them into thermodynamically steadier products. Amine type AOs such as phenolic antioxidants, which are basically utilized antioxidants, are part of the group of free radical eliminators. Usually, phenolic antioxidants (TBHQ, BHT, BHA, etc.) are mixed with biodiesel to restrict degradation. The quantum-chemical investigation of an aromatic amine N,N′-diphenyl-p-phenylenediamine (DPPD), shows that it holds its antioxidant activity even at higher temperatures [23]. Amines have a couple of p-electrons on the nitrogen particle. Accordingly, amine can be the electron giver reactant in a charge-exchange complex (relationship of two or more particles) in a relationship with oxygen-containing atoms and radicals. Additionally, the hydrogen particle from the NH bond of aromatic amine can be isolated more easily than from the OH bond of phenols because the N—H hydrogen bond is not as solid as the O—H hydrogen bond [21].

Numerous studies have been conducted on the effect of antioxidants on the oxidation stability of biodiesel, as well as their effect on engine combustion, performance and emission characterizes [12,24–33]. Recently, İleri and Koçar [28] investigated the impact of different AOs, including butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and 2-ethylhexyl nitrate (EHN), at different concentrations of 500, 700, and 1000 ppm with 20% canola biodiesel blend on the engine performance and regulated emission using a TDI (turbo charged direct) diesel engine. They note that among these antioxidants, EHN is most effective antioxidant for NOx reduction, with a reduction of approximately 4.63%, because of nitrogen presence in the antioxidant chemical structure. Hence, NOx decreases with an increase of the EHN concentration, and reverse trends occur for BHT. However, the BSFC reduction rate dramatically increased with an increase of the antioxidant concentration, and TBHQ shows better oxidation stability and the least reduction of the BSFC. However, the CO emission increased for all antioxidant concentrations. Varatharajan and Cheralathan [29] investigated the impact of two aromatic amine antioxidants (DPPD and NPPD) added with soybean biodiesel on the NOx emission in a single cylinder diesel engine and found that CO and HC increases by 10.52% and 9.096%, respectively. On the other hand, the NOx decreases by 9.35% when DPPD antioxidant is added to soybean biodiesel. In another study, Varatharajan et al. [30] observed the effect of antioxidants on the NOx emission of jatropha biodiesel with different antioxidant additives, such as 0.025%-m of p-phenylenediamine, ethylenediamine, L-ascorbic acid, α-tocopherol acetate, and BHT, in a single cylinder diesel engine (SCDE) and found that p-phenylenediamine produced, on average, 43.55% less NOx compared with pure biodiesel. On the other hand, the antioxidants significantly increased the HC and CO in all blends. Kivevele et al. [31] noticed that the heat release of diesel is the same as for stabilized biodiesel at the full load condition, and the PY antioxidant shows higher oxidation stability and lower BSFC compared to untreated biodiesel. However, the HC and CO increased by adding antioxidants. Ryu [12] studied five antioxidants with soybean biodiesel and found that the TBHQ was the most effective antioxidant for better stabilization and that there were no significant effect on combustion, smoke, HC and NOx for TBHQ throughout the experiment with varying concentration of antioxidants. H.K. Rashedul et al. [32] studied two antioxidant BHT and MBEBP with calophyllum biodiesel and found that the BHT shows better stability and reduces the NOx significantly, with a