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Impact of dicyclopentadiene addition to diesel on cetane number, sooting propensity, and soot characteristics

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ABSTRACT

Diesel engines, preferred for transportation due to high durability and efficiency, suffer from the undesired emission of harmful soot particles. The available technologies to reduce particulate emissions such as diesel particulate filters are less readily used due to the costs associated with them. Thus, novel and inexpensive method to reduce their emissions is desired. This paper presents a new hydrocarbon-based additive, dicyclopentadiene (DCPD), for diesel fuel that is shown to reduce the particulate emissions, while enhancing the cetane number for diesel. The sooting tendency of diesel blended with DCPD is studied by determining the smoke points, and the optimum blending ratio to minimize soot emissions is reported. The effect of DCPD addition on soot morphology and reactivity is also studied using different characterization techniques such as X-ray diffraction and high-resolution transmission electron microscopy for the nanostructural changes, and elemental analysis, thermogravimetric analysis, electron energy loss spectroscopy, and Fourier transform infrared for the variation in their reactivity and chemical properties. The oxidative kinetics of soots from blended fuel and pure diesel are also calculated. The results indicate that a small fraction of DCPD in diesel could act as a cetane improver, minimize soot production, and improve the physicochemical properties of soot by making it highly reactive in air to reduce its lifetime in the environment.

1. Introduction

Diesel and gasoline are widely used for transportation, and are obtained from the fractional distillation of crude oil in petroleum refineries [1]. While they witness an increase in their demand due to their high energy content and combustion efficiency, their combustion is increasing the level of pollutants in the environment [2,3]. The major pollutants include particulate matter (also known as soot), CO, NO_x, SO_x, and volatile organic compounds (VOC) [4]. Among them, soot particles of nanometer length scale are highly carcinogenic in general [5]. Continuous exposure to it can cause cancer, asthma and cardiovascular problems [6]. If present in the environment, soot also increases regional temperatures, accelerates the melting of polar icecaps, and significantly contributes to global warming [7]. Due to these concerns, and driven by the recent worldwide legislation [8,9], many control technologies have been proposed and implemented to reduce soot emissions. Several physical solutions such as modifying engine geometry to improve fuel–air mixing for soot reduction, increasing injection pressure to reduce fuel droplet size in engines, and turbocharging to increase air pressure and combustion efficiency facilitate soot oxidation in engines [10,11]. However, these techniques add to the engine manufacturing cost, and cannot completely eradicate soot formation. Diesel particulate filters can capture soot from engine exhaust [12]. However, the use of soot oxidation catalysts in them lead to their high costs and limit their usage in developing countries. Moreover, frequent filter regeneration by oxidizing the trapped soot is required to avert pressure buildup in the exhaust pipe and to prevent any decline in the engine performance [13].

Given that soot is a result of chemical reactions taking place inside engines, some chemical solutions have also been proposed in the literature. The use of oxygenated fuels such as alcohols and ethers reduce soot emission [14–19], but they lead to an increase in the emissions of NO_x, and can generate new pollutants such as aldehydes [20–23]. They also lead to the reduction in the energy density of fuels, and can cause corrosion in fuel pumps and filters [24]. Another solution is the use of metal additives to enhance soot oxidation in engines or in filters to curb

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its emission [25–27]. However, the loss of these metal nanoparticles in the atmosphere, which pose a threat to human health, and their high cost discourage their wide usage [26]. The addition of antioxidants and polymeric base additives has been also proposed to reduce particulate matter emission. However, during the storage of fuel/antioxidant mixture, a careful monitoring of chemical species and viscosity is required [28]. Moreover, the addition of polymers to fuels require optimal conditions to dissolve the polymer such as agitation and sufficiently high temperature [29,30]. Recently, several studies have shown that the addition of these kind of additives increase the NO_x and CO emissions during fuel combustion [31–33]. Another study proposed the addition of water to diesel containing a metallic additive to form an emulsified system that generates hydrogen from water molecules at high temperatures [34,35]. The hydrogen generation promotes the formation of OH radicals, which helps to reduce the soot formation rate. However, is this method, NOx emission increases [35,36], and at high engine speed, water decomposition to hydrogen is incomplete, and the results are not advantageous [37].

All the proposed solutions, described briefly above, are based on oxidizing soot inside the engines so that their concentration in the exhaust gas is well below the allowed limit. Clearly, the rate of soot oxidation (i.e. its reactivity) plays an important role in the burning of soot particles inside combustion chambers [38]. Thus, enhancing soot reactivity would provide dual benefits: (a) increased level of soot oxidation in high temperature environments inside the engines, and consequently, reduced soot concentration in the exhaust, and (b) faster regeneration of particulate filters, if they are used for capturing soot. The enhancement of soot reactivity can occur through the following means [38–40]: (a) increasing the concentration of oxygenated functional groups on soot, (b) enhancing the concentrations of radicals (active sites) on soot to allow the addition of oxidizing agents, (c) reduction in the lateral size of aromatic layers that can increase the relative amounts of highly-reactive edge to less-reactive basal carbon atoms, (d) increasing the amounts of cyclic/acyclic aliphatic groups on soot that are more reactive than aromatics, (e) increasing the amorphous content of soot, and (f) introducing the curvatures in soot nanostructures. These characteristics of soot particles are affected by the fuel type and the combustion operating conditions [38,39,41]. Thus, the desired physical or chemical modifications in soot can be achieved by carefully selecting fuel additives that produce highly-reactive soot to enhance its in-cylinder oxidation.

While fuel additives can influence soot nanostructures and enhance their reactivity to promote their burning inside the engine cylinders and reduce emissions [42–45], it is important to ensure that no new pollutants are produced while suppressing soot. The availability and cost are other major concerns that need to be addressed while proposing an additive. Most importantly, if any modifications in the engine hardware are required, it substantially adds to the cost of the vehicles, and are, therefore, not preferred. Moreover, for diesel, it is very important to maintain energy density and cetane number. For example, the addition of oxygen-rich additives to diesel suppresses soot [46], but significantly reduces fuel energy density and cetane number, and therefore, the combustion is affected drastically [47,48]. For those reasons, various substances have been added to improve the engine performance. In this direction, several cetane number improvers have been proposed in the literature, such as isoamyl nitrite [49], bis (2-methoxyethyl) ether [50], 2-ethylhexyl nitrate [51], cyclohexyl nitrate [47], and m-dioxan-5-ol nitrate [52]. These studies have showed that, when cetane number increases, higher combustion efficiency is achieved with reduced VOC, CO, NO_x, and SO_2 emissions, but soot emission increases due to reduction in the premixing of fuel and air [47]. Thus, it is imperative to study the additive effects on the blend properties as well as on the soot produced.

This study presents an investigation on a hydrocarbon, dicyclopentadiene (DCPD), for its potential to act as a soot-suppressant for diesel without reducing its cetane number and creating any new pollutants (like oxygenated compounds). DCPD was selected for this study because it is a petroleum product with comparable properties to diesel and their high miscibility. It is also present in crude oil, and thus, if found useful, it can be protected during distillation in the refinery and blended with diesel fuel [53]. Another important reason for selecting this was its chemical structure, where five-membered rings are present. It has been shown in our previous study that soot particles with curved nanostructures (PAHs) inside them significantly increase their oxidative reactivity [39]. The curvatures in soot nanostructure arise from the presence of embedded 5-membered rings in the aromatic structure. DCPD has two such rings, and it is anticipated that it may enhance the curved structures in soot and promote their in-cylinder burning. An experimental study in [54] has also showed that cyclopentadiene addition to the flames of gaseous fuels led to curved aromatic structures due to the presence of a five-membered ring in the fuel. In this paper, we report the effect of DCPD addition to diesel on cetane number, fuel sooting propensity, and the characteristics of soot particles. The oxidation kinetics of soot particles from diesel with and without DCPD will be examined, and the soot reactivity trend will be related to the physical and chemical modifications in the nanoparticles caused by DCPD addition to diesel.

2. Experimental details

The commercial diesel fuel (Grade No. 2-D S15, ASTM D975 [55]), used in the tests, was obtained from a local fuel station. The blends of diesel and DCPD (procured from Sigma–Aldrich with a purity of ≥95%) were prepared with different proportions: 5%DCPD/95%Diesel (DD5), 10%DCPD/90%Diesel (DD10), 15%DCPD/85%Diesel (DD15), and 20% DCPD/80%Diesel (DD20). A complete miscibility of the two was observed at the above-mentioned compositions with no phase separation. The important fuel properties of diesel, DD5, DD10, DD15, DD20, and DCPD were measured to understand the experimental trends. The kinematic viscosity and density of the fuel blends were measured at 40 °C at 20 °C using a Stabinger Viscometer (SVM™ 3000, Anton Paar, Austria) as per the ASTM D7042 standards [56]. The sulfur content was determined using an Energy Dispersive X-ray Fluorescence spectrometer (RX-360SH, Tanka, Japan) with ASTM D4294 standard method [57]. The ignition quality tester (IQT™, Advanced Engine Technology Ltd., Canada) using the ASTM D6890 standard method was employed to determine the Cetane number of the fuel blends [58]. Molecular weight for diesel, which is a complex mixture of hydrocarbons, was calculated using an empirical correlation from [59] that is widely used and recommended in the literature.

The combustion of the prepared blends was studied in a standard smoke point apparatus under atmospheric pressure based on ASTM D1322 method [60]. Such an apparatus is used to determine the sooting tendency of a fuel by measuring the height of the flame at its smoke point [61]. This apparatus has been used widely for soot studies [61–64], and is composed of three main parts: 1) A stainless-steel fuel reservoir of cylindrical shape having an internal diameter of 21.25 mm and length of 109 mm, and containing an air tube and wick tube inside it. 2) A cylindrical lamp body of 81 mm in diameter to protect the stable flame from any air disturbances. It also has a curved glass window, and a measuring scale to read the height of the flame. 3) A 13-cm long chimney. The reasons of choosing this apparatus is mainly due to its simplicity and the accuracy that it provides in determining the smoke point, and the ability to collect soot particles from it with some setup modifications. It has also been used in other studies [65,66] and has been observed to provide a stable flame with a fixed height. This apparatus will allow us to find the smoke point of the diesel and the blended fuels, collect soot particles from different fuels at exact flame heights.

The flame heights of pure diesel and diesel-DCPD blends were determined according to ASTM D1322 [60]. A clean and dry wick was soaked in the fuel and put inside the fuel reservoir after filling it with