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On the characteristics and reactivity of soot particles from ethanol-gasoline and 2,5-dimethylfuran-gasoline blends

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ABSTRACT

With strict environmental legislations and to reduce our dependence on fossil fuels, biofuels and their blends with hydrocarbon fuels are being seen as cleaner alternatives to meet the world's energy demand. This paper explores the effect of adding ethanol and 2,5-dimethylfuran (DMF) to gasoline on its sooting tendency as well as on the characteristics and oxidative reactivity of soot. The fuel sooting tendency is determined through its smoke point using a diffusion flame setup. Several characterization techniques such as thermogravimetric analysis, high resolution transmission electron microscopy, electron energy loss spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, elemental analysis, and Raman spectroscopy are employed to reveal the changes in the physicochemical properties of soot collected at a flame height of 25 mm. With 20% ethanol or DMF addition to gasoline, the rate of soot production, the sizes of polycyclic aromatic hydrocarbons and primary particles in soot, and its aromatic character decreased, while its amorphous character and the concentrations of oxygenated and aliphatic functional groups on it increased. These led to the increased oxidative reactivity of soot from the blended fuels. The differences in the characteristics of soot from ethanol/gasoline and DMF/gasoline blends are reported.

1. Introduction

A large portion of the world's energy demand is met through the combustion of fossil fuels, but at the expense of human health and the environment, since their combustion generates pollutants such as soot, CO, NO_x, and hydrocarbons including polycyclic aromatic hydrocarbons (PAHs) [1]. Among them, soot, a carbonaceous material, is produced during incomplete fuel combustion. It is carcinogenic, and can lead to pulmonary and respiratory diseases upon inhalation [2]. Due to its role in regional warming and the faster melting of polar icecaps, soot is recognized as the second largest contributor to global warming (the largest one being CO_2) [3]. For these reasons, it is essential to regulate their emissions from the combustion devices to abide by the strict emission standards and regulations [4].

Diesel engines emit more soot than gasoline engines, but the number of particles emitted by the latter is high, and is often higher than the prescribed limit [5]. Moreover, with the advent of the gasoline direct injection engines for a higher engine efficiency than port fuel injection engines, the problem of soot emission has aggravated [6], as the mass as well as the number of large soot particles emitted by the former is higher than the latter [7]. Thus, there is a need to develop strategies to reduce soot formation during gasoline combustion. Some techniques such as exhaust after-treatment system, addition of metal catalysts to the fuel, and fuel reformulation have been utilized to reduce soot emission. For instance, gasoline particulate filters (GPF) are used to capture soot from engine exhaust [8] in Europe due to the regulations on the number of particulates that can be emitted from gasoline engines [9]. The results show that soot emissions decrease with GPFs by around 88% without affecting the fuel economy. However, they require frequent regeneration in the presence of catalysts so that pressure does not build up in the exhaust lines of vehicles, and are expensive. Moreover, metal catalysts can be added to fuels [10] to reduce soot production, though their loss can be harmful for the environment and the human health [11]. Thus, it becomes essential to formulate new fuel blends that could lower soot emissions without modifying the engine technologies. Fuel reformulation often involves blending oxygenated and conventional fuels to facilitate the combustion process by increasing the amount of oxidizer in the combustor that leads to soot reduction.

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Several oxygenated compounds such as methanol [12], ethanol [13], butanol [14], furans [15], dimethyl carbonate [16], ethers [17], and ketones [18] have been shown to decrease soot emission when blended with gasoline. The oxygen atoms present in these fuels reduce their sooting tendency by chemical or dilution effects [19,20], or makes soot particles more susceptible towards oxidation [21]. A high soot reactivity towards oxygen is also desired for the rapid regeneration of GPFs at low temperatures in the presence or absence of a catalyst.

Among the oxygenated fuels that can be blended with gasoline, ethanol and 2,5-dimethylfuran (DMF) have gathered a lot of attention, since: (a) they can be produced from renewable feedstocks [22,23], (b) they can improve engine performance by increasing the octane number that allow engine operation at higher compression ratios for greater thermal efficiencies and fuel economy, and (c) they can suppress soot formation due to the presence of fuel-bound oxygen [24,25]. About 10–20% of ethanol can be blended with gasoline without any mechanical modifications in engines and without significantly loosing fuel energy density [26]. However, note that such small amount of ethanol in gasoline may not increase the octane number noticeably, if a low-quality ethanol is used at fuel stations for blending. Though ethanol has many advantageous properties, its use in engines is still limited due to its high latent heat of vaporization and low energy density [27]. Ethanol also has low diffusivity, and shows ignition difficulty at low temperatures [27] that can lead to incomplete combustion [28] and reduced engine performance [27]. Moreover, its production as a first-generation biofuel has some disadvantages such as the reduction in food supply, deterioration of soil quality due to fertilizer usage, extensive water usage, and other ecological issues that could lead to the destruction of habitats [29,30]. DMF, on the other hand, is high in energy density that leads to higher mileage as compared to ethanol. It has a lower heat of vaporization than ethanol that solves the cold-start problem existing with ethanol. DMF is also less volatile than ethanol that helps in its easy storage. Unlike ethanol, its mass production does not compete with food. The recent advancements in the production techniques of DMF have allowed its inexpensive synthesis from a variety of biomass and biowaste such as glucose, fructose, sucrose, starch, and cellulose [31,32]. This is important for mass production and cost efficiency. The physical properties of DMF are very similar to those of gasoline that makes it easily adoptable in conventional gasoline engines. DMF's energy density (29.6 MJ/L) is higher than that of ethanol (21.2 MJ/L), and comparable to that of gasoline (32 MJ/L) [24]. It has a higher boiling point (92–94 °C) as compared to ethanol (78 °C), and hence, a lower volatility. Furthermore, DMF is immiscible with water (thus, less probable to mix with water in transfer pipelines), and less corrosive than ethanol [33]. However, DMF has two main disadvantages: (a) it is a genotoxic compound [34], and (b) during the storage of DMF/gasoline blends, DMF may oxidize to form polar products that polymerize to form gasoline-insoluble gums [35]. This can pose a challenging problem for fuel storage. Moreover, DMF oxidation forms peroxides during storage that can present an explosion hazard when exposed to physical shock [36].

The combustion of ethanol/gasoline blends has been investigated in engines [37–40] and flames environments [41–43]. Their blends in different types of gasoline engines were shown to reduce PAH and soot emissions significantly in [44,45]. While ethanol addition to gasoline can also reduce CO and NOx emissions [46], the emission of aldehydes [47] may increase. Maricq et al. [41] analyzed the effect of adding 20%, 50%, and 85% of ethanol in gasoline diffusion flames at different fuel flow rates on soot formation. The concentration of ethanol beyond 50% in the blend resulted in an appreciable reduction in the amount of soot formed and the particle size. It was mentioned that the aspects other than the combustion chemistry such as fuel volatilization and mixing may have a substantial effect on soot formation. These results were in line with the findings of Khosousi et al. [48]. A similar effect of ethanol on ethylene soot particle size has been reported in [49], while Lapuerta et al. [50] reports a similar effect of biodiesel addition to diesel on particle size. The impact of adding ethanol to gasoline and a gasoline surrogate on PAH and soot formation in turbulent spray flames was researched by Lemaire et al. [19]. While ethanol addition reduced the quantity of soot and PAHs produced, the reactivity of soot particles also increased with increasing amount of ethanol in the mixture. They concluded that the fuel-bound oxygen played an important role in suppressing soot formation (i.e., a chemical effect), and it was not merely a dilution effect.

Several researchers have also examined the combustion properties of DMF and its blends with gasoline in engines [24,51] as well as in flames [52,53]. In [51], experiments revealed that DMF demonstrated comparable combustion and emission levels to gasoline, and it could be used in existing spark ignition engines without the need for major modifications. Also, the amount of soot emitted from DMF combustion was lower than that from gasoline. Moreover, in [24], the knocking propensity of DMF-gasoline blends was studied. It was concluded that both DMF and ethanol showed major effects on improving auto ignition resistance of gasoline. In addition, emissions such as hydrocarbons, NO_X, and particulate matter (PM) were lowered as well.

Ethanol addition to gasoline reduces the concentration of soot precursors [38], the number and mass concentrations of soot particles, and the particle diameter [45], but, depending on the operating conditions, ethanol may increase the volatile organic fraction on soot [38]. The presence of ethanol in gasoline leads to the formation of soot particles that are less compact (and thus, more reactive due to higher disorder in soot nanostructure and higher surface area) than those formed from pure gasoline [54]. While the presence of DMF in a fuel reduces the amount of soot produced [55], it enhances the oxygen content on the edges of soot [55,56]. While the increase in the oxygen content of soot is generally linked to the increased soot reactivity [57,58], Yehliu et al. [59], through their studies on soots from diesel and biodiesel, argued that there may not be a strong link between the two. Recently, the impact of DMF addition (up to 15% by volume) to diesel on soot nanostructures and reactivity toward oxygen has been explored using diffusion flames of diesel and diesel/DMF blends in our previous investigations [21]. Soot particles generated from the flames of these fuels at the same fuel flow rate in a smoke point apparatus were collected. With increasing amount of DMF in diesel, the primary particle size and the PAH length reduced in soot, whereas the aliphatic and oxygen content and the randomness in the orientations of their PAHs increased. Soot from the flames of DMF/diesel blends was more reactive as compared to diesel soot. Wang et al. [40] studied the effect of ethanol and DMF addition to gasoline on the composition of particulate matter and its oxidation rate. It was found that ethanol/gasoline blends produced the lowest amount of soot, and soot particles from these blends were the most reactive ones. This was further confirmed in [38], which also reported the reduction in PAH emissions upon ethanol addition to gasoline. In [60] as well, it was found that, in a diffusion flame, ethanol addition to gasoline by maintaining a constant fuel flow rate to the flame drastically reduced soot volume fraction.

While several investigations provide evidence of soot reduction through the addition of ethanol and DMF to gasoline, the information on the effects of this blending on soot physicochemical properties (such us reactivity, composition, morphology, and nanostructures) remains limited in the literature. The aims of this paper are: (a) to investigate the impact of the addition of DMF and ethanol on the sooting tendency of gasoline by measuring the smoke point and soot yield for each fuel, and (b) to study the characteristics of soot particles (such as the types of functional groups and chemical bonding, and the sizes of PAHs and nanostructures in soot) generated from gasoline and their blends with a fixed fuel flow rate. A diffusion flame, generated inside a smoke point apparatus (a standard instrument for measuring sooting propensity of any fuel) is used because it presents a less complex system as compared to engines, where soot formation from fuel combustion can be studied by separating the effects of engine operating conditions on it. While in gasoline engines, fuel-air mixture is mostly premixed before