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Research paper

## Size distribution, chemical composition and oxidation reactivity of particulate matter from gasoline direct injection (GDI) engine fueled with ethanol-gasoline fuel



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#### HIGHLIGHTS

• Ethanol-gasoline reduces elemental carbon in PM.

• Ethanol-gasoline increases volatile organic fraction in PM.

• Soot generated from ethanol-gasoline has higher oxidation activity.

#### ARTICLE INFO

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## ABSTRACT

Ethanol-gasoline blended fuels have been widely applied in markets recently, as ethanol reduces lifecycle greenhouse gas emissions and improves anti-knock performance. However, its effects on particulate matter (PM) emissions from gasoline direct injection (GDI) engine still need further investigation. In this study, the effects of ethanol-gasoline blended fuels on particle size distributions, number concentrations, chemical composition and soot oxidation activity of GDI engine were investigated. It was found that ethanol-gasoline blended fuels increased the particle number concentration in low-load operating conditions. In higher load conditions, the ethanol-gasoline was effective for reducing the particle number concentration, indicating that the chemical benefits of ethanol become dominant, which could reduce soot precursors such as large n-alkanes and aromatics in gasoline. The volatile organic mass fraction in ethanol-gasoline particulates matter was higher than that in gasoline particulate matter because ethanol reduced the amount of soot precursors during combustion and thereby reduced the elemental carbon proportions in PM. Ethanol addition also increased the proportion of small particles, which confirmed the effects of ethanol on organic composition. Ethanol-gasoline reduced the concentrations of most PAH species, except those with small aromatic rings, e.g., naphthalene. Soot from ethanol-gasoline has lower activation energy of oxidation than that from gasoline. The results in this study indicate that ethanolgasoline has positive effects on PM emissions control, as the soot oxidation activity is improved and the particle number concentrations are reduced at moderate and high engine loads.

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### 1. Introduction

### 1.1. Particulate matter in GDI engine

The gasoline direct injection (GDI) engine has been thriving in recent years because of its advantages in terms of fuel economy. In Europe, the market share of GDI vehicles reached 25% in 2012 [1]. Higher efficiency and higher specific power are the main superiorities of GDI engines over port fuel injection (PFI) engines [2]. However, much more particulate matter (PM) is produced from GDI engines compared with PFI engines [3]. The particle number (PN) emission of GDI vehicles can reach  $10^{13}$  #/km, which is higher than that of PFI engines [4]. In 2014, European emission standards have set PN regulation ( $6 \times 10^{11}$  #/km) for gasoline vehicles with Euro VI [5]. Furthermore, PM of GDI engine are more toxic than that of diesel engine due to the smaller size of GDI engine emitted particles

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Table 1
Geometric mean diameters of particles from typical GDI, PFI and diesel vehicles [7].

Engine type	Test	GMD (nm) nucleation mode	GMD (nm) accumulation mode
GDI	FTP-1	11.9	45.4
	FTP-2	11.5	42.3
PFI	FTP-1	8.9	42.5
	FTP-2	8.5	35.4
Diesel	FTP-1	6.6	58.4
	FTP-2	6.5	45.9

[6]. Table 1 shows the size of particles emitted from three typical vehicles [7]. The geometric mean diameters of particles from GDI engine are smaller than those from diesel engine, while they are larger than those from PFI engine. Facing these situations, PM-emission issues from GDI engines are now a widely held concern.

The high level of GDI-engine PM emissions can be explained by two mechanisms. First, although the homogeneous stoichiometric premixed combustion is adopted in GDI engines, rather than diffusion combustion, the homogeneity of the air/fuel mixture is still low because the time available for fuel evaporation and mixing with air is quite limited. It inevitably results in some regions with high temperature but insufficient oxygen in the cylinder, and this condition leads to significant endothermic pyrolysis reactions which contribute to soot formation. Second, as the fuel is injected, a certain amount of fuel in spray may impinge on the piston [8]. Due to the high temperature of piston surface, the fuel evaporates quickly and forms a vapor film, which has much higher heat transfer resistance than the liquid. The evaporation of the rest fuel on piston surface is therefore slowed down, and diffusion combustion occurs in this circumstance (pool fire) [4]. Because of the poor air/fuel mixing conditions in diffusion combustion, more PM can be generated. The major composition of engine-emitted PM includes elemental carbon (EC), organic carbon and ash [4,9]. The formation of PM is not only due to the growth of elemental carbon soot but also due to the condensation of a considerable quantity of hydrocarbons. These hydrocarbons could form particles or be adsorbed on the surface of particle aggregates [4]. Organics in PM come from compounds that are native to fuel or from compounds that are newly generated during combustion [10]. During the soot formation process, fuel molecules are fragmented into simpler molecules and act as soot precursors, such as C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. These precursors form particles nuclei with size less than around 5 nm [11]. Then hydrocarbons or hydrocarbon fragments condense on nuclei and dehydrogenation occurs in high temperature, therefore layered microstructures of elemental carbon are formed when particles grow larger. A portion of soot precursors is emitted as organic species when the soot-formation reactions are interrupted by bulk or wall quenching, particularly at low-load conditions. Because the lower combustion temperature and slower rate of fuel decomposition are not sufficient to sustain the entire reactions to form elemental carbon soot. These semivolatile organic species then condense on the surfaces of particles during the period of exhaust cooling down.

#### 1.2. Effects of ethanol on PM emissions in GDI engines

The characteristics of PM emissions in GDI engines are significantly associated with fuel properties [12]. The use of ethanol in engines have benefits in reducing life-cycle greenhouse gas emissions and harmful pollutant emissions [13]. It has been widely found that adding ethanol to PFI gasoline engines can suppress PM emissions [14,15]. However, for GDI engines, the results are divergent [16–19]. For example, some researchers [16,17] have found

Table 2

Engine specifications.		
Specifications	Value/comment	Unit
Engine type Combustion system Displacement Bore × Stroke Connecting rod length Compression ratio Catalytic converter	Four cylinder inline, 4-stroke, 4-valve Wall-guided GDI 2.0 86 × 86 145.5 9.2 Under-floor catalytic converter	L mm × mm mm

that adding ethanol to gasoline reduces the GDI engine PM emission. The experiments conducted by Zhang et al. [17] were at low speed and high load condition (2000 rpm, 210 Nm), it was found that the E10 and E20 fuels reduced PN emissions from GDI engine. While others [18,19] have reached opposite conclusions. Wang et al. [19] found ethanol addition increased the PN emissions, the experiments were at low speed and low load conditions (1500 rpm. 3.5–8.5 bar BMEP). In the chemical aspect, ethanol addition is beneficial for PM reduction because it can inhibit the formation of soot precursors, e.g., polycyclic aromatic hydrocarbons (PAHs) [20]. However, in the physical aspect, ethanol has higher heat of vaporization and lower vapor pressure compared to gasoline [21,22]. Hence the ethanol-gasoline could evaporate slower, and lead to more heterogeneous fuel/air mixture, which tends to increase PM emissions. The aim of this study is to investigate the effects of ethanol on PM characteristics of GDI engine, including size distribution, chemical composition and oxidation activity.

#### 2. Experiment setups

#### 2.1. Engine specifications and tested fuels

The engine specifications are shown in Table 2. The engine tests were conducted on a 2.0-L, four-cylinder, turbocharged GDI engine with a wall-guided injection system. A control unit for development was installed in this engine, and a typical control program that is optimized for fuel efficiency and regulated emissions based on unleaded gasoline with an octane number of #95 was written into the control unit. The properties of the gasoline and ethanol used in this study are listed in Table 3. The gasoline used in experiment is supplied by SINOPEC (China Petroleum & Chemical Corporation). For the tests of pure gasoline and E10 fuel, the engine operation mode swept speed from 1000 rpm to 3500 rpm with the step of 500 rpm, for each engine speed, four engine loads (corresponding to BMEP of 2.1 bar, 5.3 bar, 10.6 bar and 14.2 bar, respectively) are tested. Experiments on E20 fuel have chosen representative low speed (1500 rpm) and high speed (3000 rpm) conditions with four loads respectively. Due to a relatively high demands of PM samples for composition and reactivity analyses, only moderate load (10.6 BMEP) and high load (14.2 BMEP) are used for sample collection.

Fabl	e 3	
Fuel	pro	perties.

Fuel properties	Gasoline	Ethanol
Chemical formula	C <sub>2</sub> -C <sub>14</sub>	C <sub>2</sub> H <sub>6</sub> O
Molecular weight, g mol <sup>-1</sup>	98.2	46
Carbon content in mass, %	85	34.8
Density, kg L <sup>-1</sup>	0.7456	0.790
Heat of vaporization, kJ kg <sup>-1</sup>	591	838
Lower heating value, MJ L <sup>-1</sup>	44.73	21.3
RON	91	107
MON	84	89

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