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Influence of composite after-treatment catalyst on particle-bound polycyclic aromatic hydrocarbons–vapor-phase emitted from modern advanced GDI engines

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ABSTRACT

With mutagenic and cacogenic potential polycyclic aromatic hydrocarbons (PAHs) generated from engine source which have contributed to a substantial share of air toxic, so in order to characterize and eliminate the PAHs emissions of commercial engine fuelled, an experimental study has been carried out on a V6 gasoline engine working in spark-ignition (SI) and homogeneous charge compression ignition (HCCI) equipped with smart three-way catalyst converter (TWC). The particle phase and gas phase of $\mathrm{PAH_S}$ in engine exhaust, downstream and upstream the catalyst were collected by stainless-steel cartridges containing XAD-2 resin to capture PAHs species. The vapour phase and particulate bound PAHs compounds observed with two and three rings to exist almost entirely in the gas phase, on the other hands, five or more fused rings are predominantly adsorbed on soot particles, the intermediate – 4 ring $\mathrm{PAH_S}$ exist in the two $\mathrm{PAH_S}$ phases, naphthalene is the most abundant polycyclic aromatic hydrocarbon that was detected in the exhaust vapour-phase on both engine modes. The prototype catalytic converter eliminates most of the polycyclic aromatic hydrocarbons species in both $\mathrm{PAH_S}$ phases, particle phase and gas phase, except for NAP species. A prototype catalyst showed higher efficient conversion on $\mathrm{PAH_S}$ particulate-bound phase than vapor phase for both engine modes. However, when hydrogen was added upstream of the catalyst, the catalyst conversion efficiency in reducing naphthalene was increased by approximately 20%.

1. Introduction

Multi-ring organic species are called “Polycyclic Aromatic Compounds” (PAC). Within this wide range, there are species containing heteroatoms (S, N, and O) as well as those containing only carbon and hydrogen which is identified mainly in automotive emissions and automotive fuels. Polycyclic aromatic hydrocarbons (PAHs) are comprised of carbon and hydrogen atoms in two or more aromatic rings [1]. They are a group of ubiquitous persistent organic pollutants possessing carcinogenic, mutagenic, and immune-toxic properties [2]. PAHs are currently unregulated pollutants in automotive exhaust emissions, they are emitted to the atmosphere either in the vapor phase or associated with fine particles. They occur in the atmosphere due to emissions from gasoline and diesel-powered vehicles and other sources such as coal, biomass, gas, and oil combustion [3–5]. PAHs thermally very stable and therefore PAH is abundant molecules in the combustion zone. Therefore, they are always formed in combustion processes and are attributed to unburned, paralyzed, or partially oxidized fuel and lubricant oil that are transferred from the gas phase to the particulate phase by adsorption and condensation on to the existing particles or by nucleation of new particles when the exhaust cools [2]. Despite the extensive work and literature relating to the area of automotive PAHs emissions, there has been a surprising lack of definitive investigations into the link between fuels PAHs content and measured PAHs emissions. There has also been a limited amount of work investigating total PAHs emissions, i.e. particulate bound plus vapor phase emissions. Most research has, instead, concentrated on particulate bound PAHs. The nature of gasoline emissions, i.e. predominantly vapor, and the collection systems used, means that results given are closer to “totals”, or “total targeted PM and vapor phase” PAHs. However, in a real

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engine, there is always some level of in homogeneity which leads to some level of PM emissions. That PM emissions from a DI HCCI engine lie between emissions from diesel and SI engines and therefore, may not be negligible. The influence of air/fuel ratio (λ) on engine lean operation and on the emission of specific pollutants is not very well established. PM emissions are related to air-to-fuel ratio. When the air-to-fuel ratio is increased, PM diameter shifted towards smaller diameters [6]. Certain individual polycyclic aromatic hydrocarbons (PAHs) have been classified by the International Agency for Research on Cancer as carcinogenic to animals and probably carcinogenic to humans. Evidence for the carcinogenicity of some other PAHs is equivocal; for others, there is no evidence of carcinogenic potential, whilst many others have not so far been tested. PAHs have attracted much attention in the studies on air pollution recently because some of them are highly carcinogenic or mutagenic. In particular, benzo (a) pyrene has been identified as a highly carcinogenic. The occurrence of PAHs in the urban air has caused particular concern because of the continuous nature of the exposure and the size of the population at risk [7–9]. Homogeneous Charge Compression Ignition (HCCI) engines are being investigated widely because they can provide both high diesel-like efficiencies and ultra-low NOx and particulate emissions. A specific case of HCCI is gasoline-fuelled HCCI. It is attractive due to the simplicity of implementing such a technology into existing SI engines as well as the existing fueling infrastructure. However, gasoline is a complicated mixture of many different hydrocarbons which results in rather poor auto-ignition properties, there are several technical challenges that must be overcome before this promising technology is commercially viable. One significant challenge is that HCCI engines produce emissions of unburned hydrocarbon (HC), oxygenated hydrocarbons (OHC), and carbon monoxide (CO) and polycyclic aromatic hydrocarbon PAH_S. Aldehydes are mainly produced by industrial processes and combustion sources including automobile engines, the direct release of aldehydes come from internal combustion engines. Incomplete combustion of fuels and atmospheric oxidation of organic compounds are the major sources of carbonyl compounds, these pollutants have multiple sources, but motor exhaust gas is considered as one of the most important [10–12]. The gas contains specific pollutants such as alcohols and carbonyl compounds in gasoline emissions especially in HCCI engines have not been thoroughly investigated. The influence of air/fuel ratio (λ) on engine lean operation and on the emission of specific pollutants is not very well established [13–15]. The scope of such pyro synthesis reactions are very familiar – engines running on both gasoline (molecules typically in the C5–C10 range) and diesel fuel (molecules typically in the C12–C24 range) produce emissions ranging from methane (C1) to soot (upwards of a million C atoms per particle). Such reactions easily have the potential to create sufficient PAHs to account for those found in exhaust emissions [8,16]. Thus it is possible that new regulatory requirements might be considered for selected compounds including polycyclic and aldehydes, they continue to receive scientific and regulatory attention as toxic air contaminants, and carcinogens, the international agency for research on cancer (IARC) has classified formaldehyde as known carcinogen to humans [17]. However, regardless of the ability to minimize engine-out HC and CO emissions by altering engine operations or changing engine design. HCCI engines will likely require advanced exhaust emission control device, thus, engine exhaust after-treatment systems are widely considered. Catalyst technology for HC and CO removal is well understood and used in gasoline-fueled automobiles for twenty-five years. Although some oxidation catalysts were introduced much earlier, it was not until the 1980s that the Three-Way-Catalyst (TWC) was developed by which NOx, CO and HC can be converted simultaneously [18]. Catalytic converters are being widely used in automobile and considered to be the most effective technique in reducing harmful emissions from internal combustion engines. It is evidenced that future emission regulations (i.e. CO_2 limits) will see encourage HCCI and lean (i.e. O_2 presence) engine operation in addition to stoichiometric SI. A suitable exhaust after-treatment system would be required in order to reduce HC, CO, NOx and possibly PM emissions within allowable limits of the SI/HCCI dual mode engine. The current exhaust gas 3-way catalytic converters are ineffective in reducing NOx (and maybe certain hydrocarbons) under lean or HCCI engine operation conditions where the exhaust temperature is lower [19–22].

This paper describes the concentration of 16 individual PAHs in semi-volatile gas phase and in PM generated by a V6 SI/HCCI engine, PAH concentrations will be identified and quantified downstream and upstream the smart treatment catalyst. The commercial gasoline fuel was used in this investigation, in order to understand the emissions gases emitted from the HCCI engine and compare it to SI engines. It has also been an important aim of this study to see whether a prototype catalyst has the potential to reduce specifically naphthalene, acenaphthylene, acenaphthene, and fluorene emissions together with the other polycyclic aromatic hydrocarbons compounds. Analysis for both HCCI/SI engine modes, under lean and stoichiometric engine operation has been carried out. Emission measurements and PAHs analysis of the exhaust gases in the vapor phase and particulate-bound from HCCI/SI engine operation have been carried out at five engine conditions. The variables studied were engine load effect under HCCI stoichiometric operation, air to fuel ratio, HCCI and SI combustion modes under the same load, and hydrogen addition upstream of the catalyst.

2. Experimental

2.1. Engine

The multi-cylinder engine used for this research is the Jaguar AJV6 direct injection research engine having swept volume of 3 L with the specification given in Table 1. The engine Fig. 1 used in this work has been described in a previous publication [23–25]. A positive displacement supercharger is connected to the engine to be used when needed, but throughout this research natural aspiration was implemented. The engine is equipped with cam profile switching mechanism to switch between profiles required for SI and HCCI. The variable cam timing systems give the possibility of changing the cam timing of the intake and exhaust cams within a range of 60 crank angle degrees. Negative valve overlap was used to increase the amount of exhaust gas retained in the cylinder to achieve HCCI combustion. The engine is connected to an EC38 eddy current dynamometer. A DSPACE-based system coupled to a computer using MATLAB/SIMULINK software is used to control the engine parameters during operation and to record engine data.

The HCCI mode starting procedure involves a warming-up period when the engine was operated in SI mode first until the crankcase lubricant and coolant temperatures reached 90 °C. In HCCI mode the engine was operated with the throttle wide open. The temperature of the intake air was controlled by a thermal management system. Fuel flow was measured by an AVL controls gravimetric meter, and fuel direct injection pulse width is adjusted by the engine management system to maintain the required value of air/fuel ratio (Table 2).

2.2. Catalyst

The prototype 3-zone monolith catalyst (supplied by Johnson Matthey) (Fig. 1) was connected to the actual engine exhaust manifold [23]. The first zone was designed to reduce HC and NOx under lean and stoichiometric engine conditions at high temperatures > 400 °C, the second zone was designed to reduce NOx by reaction with hydrocarbon

Table 1
Engine specifications.

Engine type	Jaguar research V6, 24-V, GDI	Compression ratio	11.3
Bore	89 mm	Intake valve timing	Variable
Stroke	79.5 mm	Exhaust valve timing	Variable
Fuel	Gasoline, RON 95	Intake temperature	Variable