

Characterization of Hydrocarbon Emissions from Gasoline Direct-Injection Compression Ignition Engine Operating on a Higher Reactivity Gasoline Fuel

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ABSTRACT

Low temperature combustion engine technologies are being investigated for high efficiency and low emissions. However, such engine technologies often produce higher engine-out hydrocarbon (HC) and carbon monoxide (CO) emissions, and their operating range is limited by the fuel properties. In this study, two different fuels, a US market gasoline containing 10% ethanol (RON 92 E10) and a higher reactivity gasoline (RON 80 E0), were compared on Delphi's second generation Gasoline Direct-Injection Compression Ignition (Gen 2.0 GDCI) multi-cylinder engine. The engine was evaluated at three operating points ranging from a light load condition (800 rpm/2 bar IMEP_g) to medium load conditions (1500 rpm/6 bar and 2000 rpm/10 bar IMEP_g). The engine was equipped with two oxidation catalysts, between which was located the exhaust gas recirculation (EGR) inlet. Samples were taken at engine-out, between the catalysts, and at tailpipe locations. In addition, part of the raw exhaust was diluted and sampled for HC speciation. Canisters and sorbent membranes were used to collect volatile HCs and semi-volatile HCs, respectively. Di-nitrophenyl hydrazine (DNPH) cartridges were also used for collecting oxygenated species. Results showed overall lower HC emissions with the RON 80 E0 fuel compared to the RON 92 E10 fuel. For both fuels, the percentage of aromatic HCs was higher in the exhaust than in the fuels themselves. High aldehyde and ketone emissions were observed for both fuels. Detailed exhaust HC speciation can provide valuable information for modeling GDCI processes and eventually for determining the optimum combustion control methodologies to increase combustion efficiency and lower engine-out CO and HC emissions. In addition, HC speciation is useful for the development of robust emission control systems.

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INTRODUCTION

Various low temperature combustion (LTC) engine technologies, such as partially premixed compression ignition (PPCI) and homogeneous charge compression ignition (HCCI), have been investigated for high efficiency and low NO_x and particulate matter (PM) emissions. For example, the potential for very low fuel consumption and emissions from PPCI has been demonstrated with a diesel engine running on gasoline fuels. When a high octane gasoline fuel was injected late on the compression stroke of a boosted diesel engine operating with high EGR, the fuel injection could be completed before the start of combustion. In this process, fuel is partially but not fully premixed prior to the start of heat release [1,2]. Various gasoline-like fuels have been tested on diesel engines, and overall diesel-like efficiency has

been reported [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. However, such engine technologies often produce high hydrocarbon (HC) and carbon monoxide (CO) emissions, and their operating range is limited in part by the fuel properties. In particular, high reactivity fuels have been suggested to help improve the combustion stability at low-to-medium load operating conditions.

As part of a US Department of Energy (DOE) funded program, Delphi has been developing a multi-cylinder engine for a PPCI combustion concept with current US market gasoline fuels. Delphi uses the term Gasoline Direct Injection Compression Ignition (GDCI) in reference to this combustion process. The first generation 1.8L four-cylinder engine was operated over the full operating map with

PCCI combustion without the need for any combustion mode switching with a RON 92 E10 gasoline. A second generation engine has been developed, and high diesel-like fuel efficiency low emissions were demonstrated on engine dynamometer testing [15, 16, 17, 18, 19, 20, 21].

In this study, two different fuels, a US market gasoline containing 10% ethanol (RON 92 E10) and a high reactivity gasoline (RON 80 E0), were compared on a Delphi's second generation Gasoline Direct-Injection Compression Ignition (Gen 2.0 GDCI) multi-cylinder engine [21]. This engine was equipped with two close-coupled oxidation catalysts with the exhaust gas recirculation (EGR) inlet located in-between. Emissions were examined at the engine-out, between the catalysts, and the tailpipe locations to assess the exhaust conditions and performance of the prototype gasoline oxidation catalysts (GOC). Detailed HC speciation was performed to help better understand the HC species measured by emission benches and Fourier transform infrared spectrometer (FTIR.)

Speciation of HC emissions can help to understand fuel utilization in GDCI combustion. Combustion efficiency is typically measured by quantifying CO and unburned HCs. This can be misleading in a couple of instances with PCCI. First, if the HC makeup of the unburned HCs doesn't mirror the fuel composition, then the combustion process is preferentially utilizing certain fuel HCs over others. Second, if methane is formed during combustion, due to reduction of methyl radicals or formaldehyde with H, then the combustion efficiency can also decrease [27]. HC speciation has been used in other recent studies of RCCI to identify exhaust species with HC species typically dominated by unburned species from both the reactive and non-reactive fuels [28]. In this study, the HC species of the engine exhaust are used to compare and contrast GDCI engine operation with a conventional gasoline fuel (RON 92 E10) and with a higher reactivity gasoline fuel (RON 80 E0).

EXPERIMENTAL SETUP

Engine and Instrumentation

Table 1. Engine specifications

Engine Type	4-valve Compression Ignition
Displacement	1.8 L
Bore x Stroke x Rod	82.0 x 85.2 x 148.2 mm
Compression ratio	~15:1
Cylinder Head	Shallow Pentroof 10 degree
Swirl and Squish	Minimum Mixture Motion
Piston	GDCI Omega
Oil Jets	Enhanced Individual-Cylinder
Cylinder Pressure Rating	200 bar
Fuel Injection System	Central Mount, 400 bar GDI Multi-hole
DOHC Type II Valvetrain	Exhaust Only- Exhaust Rebreathing
Boost System	2-Stage (Turbo and Supercharger)
EGR System	Cooled Low Pressure EGR Loop
Thermal Management	Low and High Temperature Loops
Aftertreatment	2 Gasoline Oxidation Catalysts

The experiments were performed with a Gen 2.0 GDCI 1.8-liter four-cylinder engine. Engine specifications are summarized in [Table 1](#) [21]. The engine was operated with a Driven engine controller based on National Instruments hardware and LabView software. All the experiments were performed on an engine dynamometer at Aramco Research Center – Detroit to investigate the characteristics of HC emissions during GDCI combustion process as well as the effects of fuel's autoignition quality on HC emissions.

Fuels

A US market gasoline (RON 92 E10) and a higher reactivity gasoline (RON 80 E0) were tested in this study in order to characterize the fuel's reactivity effects on HC emissions. The RON 92 E10 gasoline, representative of US grade market "regular" gasoline, has been used for GDCI research for several years [15, 16, 17, 18, 19, 20, 21]. Based on the results from the previous study performed with Gen 2.0 GDCI single-cylinder research engine, the RON 80 E0 gasoline was chosen and compared with the RON 92 E10 in this study because the RON 80 E0 gasoline exhibited much better performance and emissions behavior at low load conditions while achieving similar performance and emissions behavior at higher load engine operation compared to the RON 92 E10 gasoline [20]. The major fuel properties are listed in [Table 2](#).

Table 2. Fuel properties of tested fuels

Fuel	RON 92 E10	RON 80 E0
Research Octane Number	92.6	80.3
Motor Octane Number	83.0	77.9
Derived Cetane Number	21.0	26.3
Specific Gravity at 15.56 °C	0.720	0.745
Gross Heating Value [MJ/kg]	45.08	46.76
Net Heating Value [MJ/kg]	42.09	43.68
Carbon [wt%]	81.90	85.49
Hydrogen [wt%]	14.07	14.51
Oxygen [wt%]	4.03	0.00

[Figure 1](#) shows the distillation characteristics of two tested fuels. The dotted grey area in the figure represents the distillation range of typical US market gasoline fuels [22]. The RON 92 E10 gasoline used in this study was at the lighter end of the distillation range of typical US market gasolines because this fuel was procured during the winter season. The RON 80 E0 gasoline showed similar initial and final boiling temperatures as the RON 92 E10 gasoline, while the RON 80 E0 gasoline showed less volatility throughout the distillation curve than the RON 92 E10 gasoline.

The analysis of fuels' chemical compositions was performed by using Fluorescent Indicator Adsorption (FIA) method (ASTM D1319). The results of two tested fuels were compared in [Figure 2](#). The RON 80 gasoline shows higher concentration of the saturated compositions (such as paraffins, isoparaffins, and naphthenes) than the RON 92 E10; that is, the RON 80 E0 gasoline is consisted of mostly paraffinic components. Both fuels contained similar level of aromatic contents while much lower concentration of olefins was observed in the RON 80 E0 fuel.

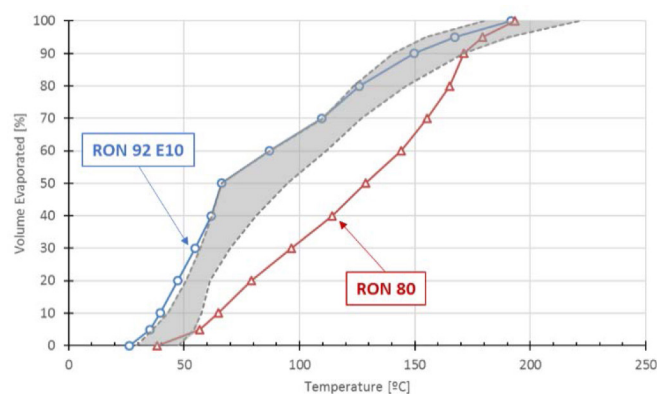


Figure 1. Distillation characteristics of tested fuels

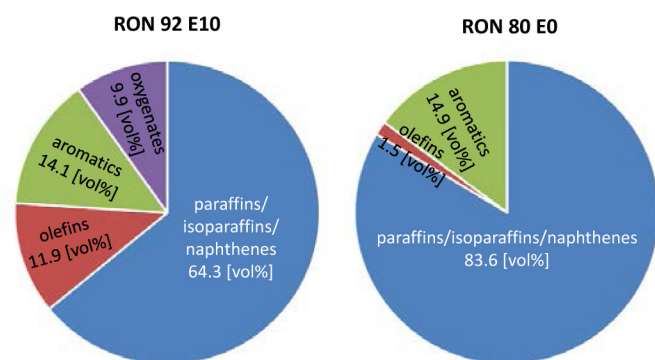


Figure 2. Chemical compositions of tested fuels

Engine Operating Points

The Gen 2.0 GDCI multi-cylinder engine was tested on a steady-state dynamometer at three engine operating conditions covering from light load to medium load range. The engine was optimized by manually adjusting various control parameters. Much more detail on the engine operation is available in a companion study that focuses on the combustion characteristics [23]. Table 3 lists the three engine operating conditions focused in this study. At the lowest load condition, 800 rpm / 2.0 bar gross indicated mean effective pressure (IMEP_g), intake boost was not required for either fuel and the engine was able to operate at naturally aspirated condition with the supercharger declutched. An exhaust rebreathing strategy was applied for the two lower load engine operating conditions, 800 rpm / 2.0 bar IMEP_g, and 1500 rpm / 6.0 bar IMEP_g, and cooled external EGR was only used for 2000 rpm / 10 bar IMEP_g engine operation. All operating points were fuel lean.

Table 3. Engine operating conditions

Fuel	800 rpm	1500 rpm	2000 rpm
RON92	No external EGR Max rebreathing	~10% EGR Max rebreathing	~33% EGR No rebreathing
RON80	No EGR No rebreathing	No EGR No rebreathing	~38% EGR No rebreathing

Emission Sampling

Emission Benches and FTIR

Exhaust emissions were sampled at three locations: engine out (EO point) about 15 cm before the entrance to the first gasoline oxidation catalyst (GOC), between the two GOC's (BC), and tailpipe (TP point) about 30 cm downstream from the exit of the second GOC. Figure 3 illustrates the sampling and dilution schemes. The raw exhaust was routed through high temperature ball valves and heated lines (190 °C) to a heated manifold (190 °C) for distribution to instrumentation and the dilution sampler. This report focuses on the engine out emissions and a later report will detail the oxidation catalyst effects.

Exhaust emissions were measured by Horiba Mexa-7500D emissions bench. A standard heated chemiluminescence detector (CLD) and a flame ionization detector (FID) were used for measuring NO_x and HC emissions, respectively. CO and intake/exhaust CO₂ emissions were measured using non-dispersive infrared (NDIR) instruments. A paramagnetic detector (PMD) was used to measure O₂ concentration. Both a smoke meter (AVL 415SE) and a micro soot sensor (AVL 483) were used to collect engine-out PM information, filtered smoke number (FSN) and soot concentration (mg/m³), respectively.

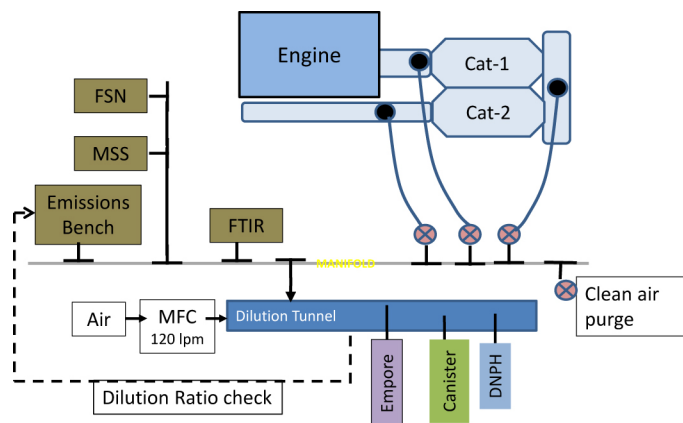


Figure 3. Diagram of sampling setup. MSS = microsoot sensor. FSN = smokemeter. MFC= Mass Flow Controller. DNPH=di-nitrophenyl hydrazine cartridge. Pumps and flowmeters not shown.

In addition, an AVL SESAM i60 FTIR unit with an optical path length of 5.11 m and a liquid-N₂ cooled Mercury Cadmium Telluride (MCT) detector was used to examine HC emissions. The gas cell was operated at a pressure of 800 mbar and a temperature of 191 °C. Measurement scans were performed at 1 Hz with a spectral resolution of 0.5 cm⁻¹.

The standard AVL "Gasoline 1 Hz" analysis method (referred to hereafter as the Gasoline method) was used to quantify exhaust gas composition and perform partial speciation of HCs. The FTIR compounds of primary interest are C2/C3 hydrocarbons (e.g., acetylene, ethylene, propene), oxygenated hydrocarbon species (e.g., ethanol, formaldehyde, acetaldehyde), and nitrogen-containing species (e.g., NO, NO₂, N₂O). General HC groups with carbon numbers higher than 3 (>C3) can also be quantified using broadband spectral features within the method. These species include aromatics, normal paraffins (nC5) and iso-paraffins (iC4+). All of the emissions

from the FTIR are listed as wet concentrations. Table values are the result of 1 Hz scanning and quantification rates over a sampling period of 2 minutes.

It is important to note that the FTIR analysis method has been developed to measure the exhaust composition of gasoline spark-ignition engines. As such, applying this method to quantify emissions from advanced, low-temperature-combustion (LTC) engines that are run with alternative fuels may result in a misrepresentation of actual concentrations. For example, it is challenging to differentiate the FTIR spectral features of species with similar functional groups, such as formaldehyde (HCHO) and acetaldehyde (CH₃CHO). In fact, some of the species that are more relevant to LTC running on alternative fuels are not included in the Gasoline method. As a result, using the standard Gasoline method broadband spectral features to quantify unburned hydrocarbon species often leads to a poor carbon balance when compared to FID measurement.

For this reason, we have developed a new method (referred to hereafter as the LTC method), which include other oxygenated hydrocarbon species that may be present during the LTC, such as acrolein (CH₂CHCHO) and carboxylic acids. In this project, HC speciation by FTIR methods are compared with more traditional integrated sampling approaches for detailed HC speciation described below to improve the FTIR analysis technique for LTC and alternative fuels.

Dilution Sampling for Sample Collection

The dilution sampler was modeled after the systems used in several previous studies [24, 25, 26]. An ejector pump was used to sample raw exhaust from the exhaust manifold and dilute the sample flow with HEPA-filtered, HC-free air. Dilution ratio was monitored by measuring the CO₂ in the exhaust and the CO₂ in the diluted exhaust. Di-nitrophenyl hydrazine (DNPH; Waters Sep-Pak®) cartridges were used to sample aldehydes and ketones, and pre-evacuated canisters (Entech) were used to sample C₅-C₁₂ gases. Because semi-volatile HC species (SVOC) can be difficult to capture, a separate collection system was set up for these based on methods developed in our laboratory [27]. An in-series dual 47mm filter holder was equipped with a PTFE membrane filter (Pall Sciences Teflo™ 2.0 µm) in the front portion to remove solid particles and a solid phase sorbent filter (Empore® SDBXC) in the rear portion. In contrast to polyurethane foam plugs (PUF), which require pre-cleaning and large amounts of solvent for extraction, Empore® disks have a simple extraction step and low background. The SVOCs were captured on the styrene-divinyl benzene solid phase embedded in the Empore® disk.

Detailed HC Speciation

The DNPH cartridges are eluted with HPLC-grade acetonitrile to a final volume of 3.0 ml. 7 µl of the eluent is analyzed with HPLC (Agilent 1100) equipped with a 3.1X100 mm C₁₈ column and UV detection. Depending on the total HC concentration, between 100 ml and 500 ml of the canister gas is concentrated (Entech 7100 pre-concentrator) and then analyzed with GC-MS. In Equation 1, The individual species concentrations in the raw exhaust (c_i) are then determined from the total mass of the species, i (m_i) measured, the

volume of dilute exhaust sampled through the DNPH cartridge or “injected” from the canister (v), and the dilution ratio (DR). For direct comparison to FTIR data, the ppmC₁ concentrations (C_{C1}) are determined from the ideal gas law as shown in Equation 2, where MW_i = the molecular weight of compound i, c_i = concentration determined with Eq. 1 in µg/L, p = the atmospheric pressure (atm), R = the gas constant (0.082 L·atm/mol·K), T = the sample temperature (°K), and CN_i = number of carbon atoms in a molecule of compound i.

$$c_i = \frac{m_i}{v} \cdot DR$$

Eq. 1

$$C_{C1} = \frac{c_i}{MW_i \cdot p} \cdot R \cdot T \cdot CN_i$$

Eq. 2

The SVOCs are captured on the Empore® disk, and eluted with a 25 ml of a 50:50 mixture of hexane and ethyl acetate. The extract volume is blown down gently under N₂ to 1 ml, and then 2 µl of extract is analyzed by GC-MS. The volume of dilute gas sampled and the dilution ratio are used to calculate the concentrations of the different species as in Eq. 1.

RESULTS AND DISCUSSION

Fuel Effects on Emissions

The effects of fuels on engine-out criteria emissions from the standard benches are summarized in Table 4. The RON 80 E0 had lower HC emissions at the low to medium load points (i.e., 800 rpm/2 bar IMEP and 1500 rpm/6 bar IMEP) compared to the higher load point. CO emissions are lower for the RON80 E0 fuel except at the low-load point. The NOx and PM emissions for RON80 E0 are lower than the RON 92 E10 at all three operating points.

Figure 4 shows that HC species are effectively, but not completely oxidized over the two oxidation catalysts for both fuels: 88-95% conversion for the RON 92 E10 fuel and 91-94% conversion for the RON80 E0 fuel. There is almost no conversion of HCs for 800 rpm/2 bar IMEP point, however. Oxidation catalysts are typically very effective for the oxidation of CO and HCs once they reach the operating temperature (e.g., >200°C), but exhaust temperatures at the 800 rpm/2 bar IMEP point were lower than that (Table 4.) However, high levels of CO and HCs can be difficult to oxidize, and may require larger oxidation catalysts and/or higher catalyst loadings.

Table 4. Fuel effects on engine-out emissions from standard benches

Fuel	RON 92 E10			RON80 E0		
	800/2	1500/6	2000/10	800/2	1500/6	2000/10
Load	800/2	1500/6	2000/10	800/2	1500/6	2000/10
CO	7797	7628	5524	8741	4100	2061
THC	6074	3693	2136	4618	2844	2142
CH ₄	120	67	39	94	31	29
NOx	7	13	31	4	7	14
SMK	0.07	0.13	0.16	0.04	0.06	0.13
MSS	0.47	1.43	1.93	0.15	0.54	1.03
T EO	124	330	351	138	308	350
T Cat1	180	327	359	171	338	374
T Cat2	171	379	389	166	355	395

*CO, THC, CH₄, NOx in ppm; SMK in FSN; MSS in mg/m³ (at 100°C)