

Speciated Engine-Out Organic Gas Emissions from a PFI-SI Engine Operating on Ethanol/Gasoline Mixtures

Kenneth Kar and Wai K Cheng
Massachusetts Institute of Technology

Copyright © 2009 SAE International

ABSTRACT

Engine-out HC emissions from a PFI spark ignition engine were measured using a gas chromatograph and a flame ionization detector (FID). Two port fuel injectors were used respectively for ethanol and gasoline so that the delivered fuel was comprised of 0, 25, 50, 75 and 100% (by volume) of ethanol. Tests were run at 1.5, 3.8 and 7.5 bar NIMEP and two speeds (1500 and 2500 rpm). The main species identified with pure gasoline were partial reaction products (e.g. methane and ethyne) and aromatics, whereas with ethanol/gasoline mixtures, substantial amounts of ethanol and acetaldehyde were detected. Indeed, using pure ethanol, 74% of total HC moles were oxygenates. In addition, the molar ratio of ethanol to acetaldehyde was determined to be 5.5 to 1. The amount (as mole fraction of total HC moles) of exhaust aromatics decreased linearly with increasing ethanol in the fuel, while oxygenate species correspondingly increased. These results suggest that the change in ethanol and aromatics exhaust emissions were due to fuel replacement. It was also found that the oxygenate fraction of total hydrocarbons (as ppmC1) depended mostly on the ethanol fuel content, not on engine speed and load. Therefore, a simple FID response correction equation was developed and validated. A FID reading can now be corrected to 90% accuracy when a PFI-SI engine is fuelled with gasohols.

INTRODUCTION

With the Energy Independence and Security Act in the US and renewable fuel mandates in the world, ethanol has been increasingly introduced as a supplement to petroleum-based gasoline (gasohol). The future use of ethanol may increase further when the process of

converting ethanol from plant celluloses becomes commercially viable. Although ethanol has been supplied as a low concentration blend to gasoline (E10), high concentration blends (E85 or E100) can be found in the US and Brazilian markets. It is therefore important to assess the effects of ethanol-gasoline blends on engine emissions.

A gasoline engine emits organic gases comprising both partial oxidation products and unburned fuel. Organic gas emissions are usually measured using a flame ionization detector (FID). When an engine is fueled with an ethanol-gasoline mixture, some ethanol will be left unburned and ends up in the exhaust. The amount is especially significant during cold start. Other oxygenates (as partial reaction products of ethanol) are also present. It is well documented [1] that the FID response is proportional to the carbon atom concentrations for hydrocarbons. The response for oxygenates, however, is significantly lower. Consequently, if a FID is used to measure the emissions of an engine fueled with ethanol and gasoline mixtures, the readings for total carbon concentrations will be underestimated. The extent of underestimation depends on the proportion and types of oxygenates.

The objective of this study is to quantify the speciated organic gas emissions from a modern SI engine operating on gasohols. From the speciated data under different operating conditions, a correlation is developed to correct for the FID underestimate of exhaust organic gas carbon count due to the presence of oxygenates.

METHODOLOGY

Exhaust gas has been speciated by using gas chromatography (GC) [2–8], high performance liquid chromatography [9], Fourier transform infrared spectroscopy (FTIR) [10, 11], and photoacoustic spectroscopy [12]. FTIR and photoacoustic spectroscopy can identify specific species in the exhaust gas, such as ammonia and ethanol, but the number of species that can be identified at any one time is limited. More problematic is that the measurements have been reported to be sensitive to cross interference, i.e. the measured concentration of a particular species may change in the presence of other species. For instance, Loo et al. [12] evaluated a commercial product (Innova 1312) based on photoacoustic spectroscopy and reported that compensation for ammonia and carbon dioxide was required to get accurate ethanol concentration.

Exhaust gas is a complex mixture. It contains ultrafine particles, combustion products, partial reaction products and unburned fuel. There are more than a hundred species which can be separated and measured by a GC. This study adapted the gas chromatographic method developed in the Auto/Oil Air Quality Research Program (AQIRP) [4, 5] for speciation. Compared to other methods, the adapted method has the following advantages:

- A GC library containing the retention time of 150 species is available; authentic standards were used to establish the library
- The accuracy and reliability of this method has been evaluated and tested by several independent laboratories
- It was used for over 8000 GC analyses; so most practical issues had been identified and resolved.
- The GC system required is relatively simple to set up and maintain

Only a brief description of the analytical method will be given here. A detailed description can be found in [4, 5]. Exhaust GC analysis was performed on a Hewlett Packard Model 5890C Series II GC. Exhaust gas samples were introduced into a six-port Valco switching valve. This valve allowed a fixed volume of gas sample to be maintained at a known pressure and temperature. It also injected samples into the GC in milliseconds, so that retention times were highly repeatable. Samples were then directed through a split injector. Only 1/5 of every sample entered the column; the remainder was vented out. The gas mixture was separated in a 60-meter column in 54 minutes. Each species was individually detected using a FID detector. Unlike the original method in [4], a make-up gas of helium was used instead of nitrogen. This only changed the sensitivity of the detector (counts/ppmC1), which was accounted for in calibration. More details are given in the Quantification section. Table 1 lists the GC parameters used in this study.

Table 1. Summary of GC analysis parameters

Instrument	HP5890 Series II Gas Chromatograph
Column	60 m DB-1 (Agilent) 0.32 mm ID, 1 µm film thickness
Sample Loop	2.0 mL
Sample Loop and valve temperature	120°C
Split ratio	5.2:1 (injection volume = 0.38 mL)
Injector temperature	200°C
Carrier gas	Helium >99.999%, 145 kPa to get 7.0 mL/min at -80°C
Detector Type	FID
Detector temperature	300°C
Detector hydrogen	>99.999%, 110 kPa
Detector air	<0.1% total hydrocarbon, 285 kPa
Detector make-up gas	Helium, >99.999%, 275 kPa to achieve 32 mL/min
Separation conditions	-80°C for 0.01 min -80°C to -50°C at 20°C/min -50°C for 2.5 min -50°C to 250°C at 6°C/min

This method can identify a total of 163 species comprising C1-C12 hydrocarbons, alcohols, aldehydes and ethers,. The GC library was compiled in phase I of AQIRP and was revised in phase II. This study utilized the revised library which covers most of the hydrocarbon species emitted from gasoline fueled vehicles. In this study, 80-90% of the species could be identified which on average covered 95% of the total hydrocarbon mass. The detection limit was 0.05 ppmC1 as determined in AQIRP.

IDENTIFICATION – Hydrocarbons were identified by their retention times. The GC was calibrated using a 23 component gas reference (CRC Mixture #4) consisting of normal alkanes from C1-C12 and other representative compounds. See Table 2. The gas standard establishes the retention times of normal alkanes which are used to calculate a retention index (RI) for each species.

$$RI = 100n + 100 \frac{t_x - t_n}{t_{n+1} - t_n} \quad (1)$$

where,

- t_x = retention time of unknown species, x
- t_n = retention time of n-alkane eluting prior to x
- t_{n+1} = retention time of n-alkane eluting immediately after x
- n = carbon number of n-alkane with retention time t_n

The species identification was done by matching the calculated RI to the ones in the GC library.

Table 2. Calibration mixture for GC analysis

Peak number	Compound	Concentration (ppmC1 ± 95% confidence interval)	Retention index
1	Methane	4.98 ± 1.8%	100.0
2	Ethene	3.03 ± 2.7%	158.1
3	Ethyne	1.10 ± 1.7%	187.3
4	Ethane	4.96 ± 1.2%	200.0
5	Propane	9.16 ± 1.4%	300.0
6	2-methylpropene	4.99 ± 2.9%	390.5
7	1,3-butadiene	5.21 ± 3.1%	395.1
8	n-butane	5.18 ± 3.1%	400.0
9	n-pentane	5.01 ± 1.9%	500.0
10	n-hexane	4.72 ± 2.5%	600.0
11	Benzene	4.66 ± 2.3%	649.7
12	2,2,4-trimethylpentane	4.93 ± 2.6%	689.9
13	n-heptane	4.92 ± 2.5%	700.0
14	Toulene	5.08 ± 3.0%	756.8
15	n-octane	5.01 ± 2.9%	800.0
16	p-xylene	5.13 ± 5.0%	862.7
17	o-xylene	5.15 ± 5.1%	885.1
18	n-nonane	5.01 ± 2.9%	900.0
19	1,2,4-trimethylbenzene	3.16 ± 3.7%	989.0
20	n-decane	5.36 ± 3.1%	1000.0
21	n-undecane	4.98 ± 4.2%	1100.0
22	n-dodecane	3.75 ± 3.3%	1200.0
23	n-tridecane	3.0	1300.0

EXHAUST SAMPLING – In the AQIRP vehicle tailpipe emissions were diluted and collected in a Tedlar bag. The sample was pulled to the sample loop by applying a vacuum to the downstream. Since raw engine exhaust is the subject of this study, a different sampling method was used. Engine exhaust was taken from a mixing tank downstream of the exhaust pipe. It was transferred to an exhaust gas sample storage unit via a heated sampling line at 150°C. One of the sixteen sampling cylinders and its associated components are shown in Figure 1.

The sampling cylinders were initially evacuated through a 3-way valve at the top of the sampling cylinder. A continuous stream of exhaust gas was drawn through the splitter via a solenoid valve and bypass circuit using a vacuum pump. During sampling the three-way solenoid valve was energized, and exhaust gas was sucked into the sample cylinder due to the pressure gradient. The solenoid valve was only opened briefly so that the final tank pressure was at about 15 kPa. The low pressure ensured that water and heavy hydrocarbon would not condense. In addition, the whole system was heated to 150°C.

Immediately after sample collection, the cylinder was filled with research-grade nitrogen (>99.9999%) to 300 kPa. Therefore, the exhaust concentration was diluted 18-20 times. The dilution was conducted with a system containing a pressure transducer (MKS Baratron

629B), a separate vacuum pump to evacuate lines and valves and a 3-way valve to switch between evacuation and nitrogen filling. With 16 sampling cylinders, exhaust gas under different engine conditions could be collected at the same time before GC analysis. Most samples were analyzed within a day.

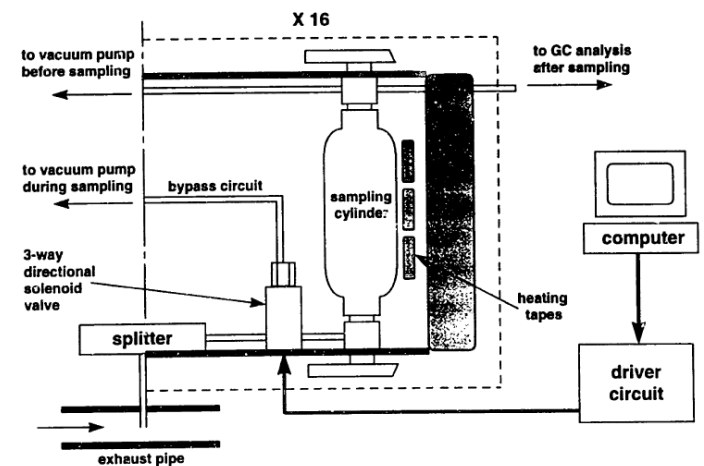


Figure 1. Schematic of exhaust gas sampling system. Reproduced from [13]

EXHAUST ANALYSIS PROCEDURE – The GC was always calibrated with the gas standard before analyzing any sample. The sampling loop in the GC was purged with nitrogen (>99.999%) for 2 minutes to ensure that there were no residual sample from a previous test. The sample cylinder with the diluted exhaust sample was connected to the GC inlet via a 1-m heated transfer line at 60°C. The temperature was limited by the line material which was made out of Teflon — too high a temperature could have degraded the Teflon which would have introduced extraneous hydrocarbons to the sample. The 3-way valve at the top of the sampling cylinder was then opened to the outlet port, which allowed the exhaust sample to flow through the sampling loop for 10 seconds. Then the outlet side of sample loop was shut and the sampling pressure recorded (about 150 kPa abs). The sample was trapped in the sample loop for 4 minutes before injecting into the GC. The trapping time was to allow the sample to reach a thermal equilibrium with the sampling loop, which was kept at 120°C.

QUANTIFICATION – The FID detector in the GC is a calibrated instrument. The HP ChemStation software version A.10.02 integrates the area under each peak and stores the results as area counts. So a species i with concentration $[s_i]$ has an area count A_{si} . A response constant k_i can be calculated as:

$$k_i = \frac{A_{si}}{[s_i]} \quad (2)$$

Typically the response constant ranges from 900-1000 area counts/ ppmC1. Note that k_i is specific to sample loop temperature (T_s) and pressure (p_s). Consider now an exhaust gas species j which returns

in the chromatogram. The area count needs to be normalized to the same state as in the calibration, that is

$$A_j^* = A_j \frac{p_s}{p} \frac{T}{T_s} \quad (3)$$

where p and T are the exhaust gas pressure and temperature in the sample loop. For those exhaust species found in the gas standard, the concentration $[x_i]$ can be determined as

$$[x_i] = \frac{A_j^*}{k_j} \quad (4)$$

For other hydrocarbon species, propane's response constant is used. Ethanol and acetaldehyde are oxygenates, so their FID response is lower than those of C2 hydrocarbons. The response of FID to ethanol was measured [14] in the range 15–1500 ppm by volume. The results showed that the response in ppmC1 was 0.74 of that of propane:

$$\alpha_{\text{Ethanol}} = \frac{k_{\text{Ethanol}}}{k_{\text{Propane}}} = 0.74 \quad (5)$$

The response of acetaldehyde is not reported in the literature. The reduction in FID response of alcohol is due to C being bonded to O in the R-O-H group (R stands for an alkyl) [1]. Since ethanol and acetaldehyde are primary alcohols, they should have a similar reduction in FID response. In this study, it is assumed that the response factor for ethanol and acetaldehyde are the same.

EXPERIMENTAL SET UP AND PROCEDURES

A 1.8 L I-4 DOHC spark-ignition engine was modified for single-cylinder operation. See Table 3 for the engine specifications. The engine has 4 valves per cylinder and features a centrally located spark plug, a pent-roof combustion chamber, and a flat piston. All these features are considered to be representative of a modern spark-ignition engine. The intake and exhaust systems were modified to separate the flow through one cylinder from the other three. Figure 2 shows a simplified view of the engine setup, instrumentation and hydrocarbon measurement systems.

Table 3. Engine specifications

Displacement	442.3 cm ³
Compression ratio	11.0
Bore	80 mm
Stroke	88 mm
Connecting rod length	140.5 mm
Inlet Valve Timing	IVO: 5 deg bTDC IVC: 51 deg aTDC
Exhaust Valve Timing	EVO: 26 deg bBDC EVC: 2 deg bTDC

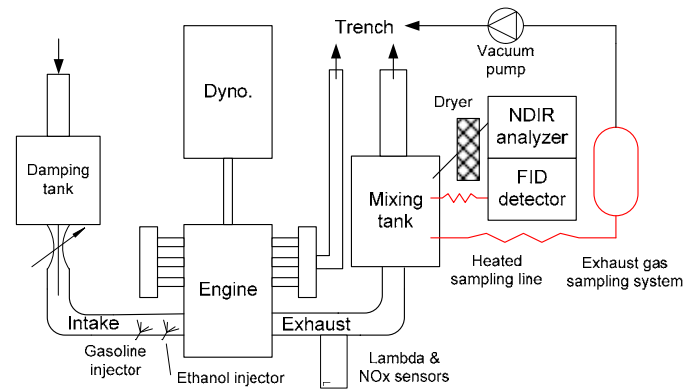


Figure 2. Schematic of experimental setup

A Kistler 6051A piezoelectric pressure transducer and a Kistler 5010 charge amplifier were used for in-cylinder pressure measurements. In-cylinder pressure was pegged to the manifold absolute pressure at BDC at the intake stroke.

Table 4. Chevron UTG91 gasoline properties

Property	Value
Density at 15.6°C	739.6 kg/m ³
Reid vapor pressure	63.4 kPa
Sulfur	7.6 ppm
Hydrogen / Carbon ratio	1.93
Lower heating value	43.20 MJ/kg
Research Octane No.	90.5
Motor Octane No.	83.0
Aromatics	26.5% liquid vol.
Olefins	4.0% liquid vol.
Saturates	69.5% liquid vol.
Oxygenates	0.0% liquid vol.
Benzene	0.65% liquid vol.

A research grade gasoline, Chevron Phillips UTG91 was used in this study. The fuel properties are given in Table 4. The ethanol (Pharmco-Aaper 200 proof) was anhydrous with a typical purity of 99.98%. The gasoline and ethanol were injected into the intake port by two separate injectors by two independent fuel systems (see Figure 2). Different ethanol-gasoline mixtures can be created by metering the injection pulse width of the corresponding fuels. The injectors were volumetrically calibrated offline.

Exhaust gas was drawn from a mixing tank about 2 m from the exhaust port. Sampling from a mixing tank eliminated any spatial and temporal inhomogeneity in the sampling process. Unspeciated organic gas emission was measured using a Horiba NDIR analyzer (MEXA-554JU) and a Combustion fast FID analyzer (HFR400). The NDIR analyzer only accepted dry samples, so exhaust gas was chilled and its water vapor was condensed before admitting it to the analyzer. The fast FID analyzer took wet samples directly with a heated sampling tube to avoid condensation.. The instruments were calibrated with 2400 ppm (±1%) propane before and after the test. The calibration was found to be consistent within 1-2%.