MIT Libraries | DSpace@MIT

MIT Open Access Articles

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

Massachusetts Institute of Technology

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

Kenneth Kar, Wai K Cheng
Massachusetts Institute of Technology

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 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 ethanol and aromatics detected were from unburned fuel trapped in crevices. 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 adaped 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 complied 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)
1	Methane	4.98 ± 1.8%
2	Ethylene	3.03 ± 2.7%
3	Ethyne	1.10 ± 1.7%
4	Ethane	4.96 ± 1.2%
5	Propane	9.16 ± 1.4%
6	2-methylpropene	4.99 ± 2.9%
7	1,3-butadiene	5.21 ± 3.1%
8	n-butane	5.18 ± 3.1%
9	n-pentane	5.01 ± 1.9%
10	n-hexane	4.72 ± 2.5%
11	Benzene	4.66 ± 2.3%
12	2,2,4-trimethylpentane	4.93 ± 2.6%
13	n-heptane	4.92 ± 2.5%
14	Toulene	5.08 ± 3.0%
15	n-octane	5.01 ± 2.9%
16	p-xylene	5.13 ± 5.0%
17	o-xylene	5.15 ± 5.1%
18	n-nonane	5.01 ± 2.9%
19	1,2,4-trimethylbenzene	3.16 ± 3.7%
20	n-decane	5.36 ± 3.1%
21	n-undecane	4.98 ± 4.2%
22	n-dodecane	3.75 ± 3.3%
23	n-tridecane	3.0

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. 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.
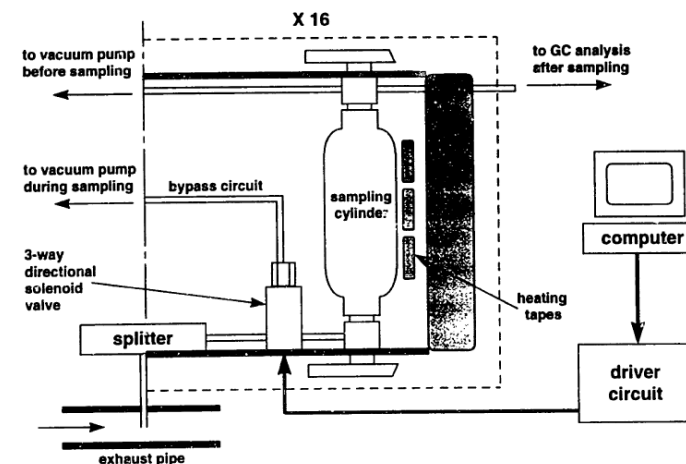

Figure 1. Schematic of exhaust gas sampling system. Reproduced from [13]

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:

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

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

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

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

$$[x_i] = k_j A_j^* \qquad (4)$$

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:

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

The response of acetaldehyde is not reported in the literature. The value, however, may be deduced from the nature of the ionization chemistry. The carbon in the carbonyl bond in acetaldehyde would not be able to contribute to a chemi-ionized ion [1]. Thus the reponse function is $\alpha_{\text{acetaldehyde}} = 0.5$.

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

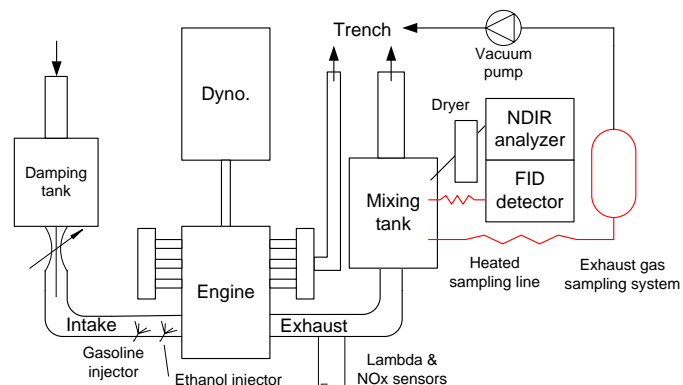| Inlet Valve Timing	IVO: 5 deg bTDC
	IVC: 51 deg aTDC
Exhaust Valve Timing	EVO: 26 deg bBDC
	EVC: 2 deg bTDC

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. Un speciated organic gas emission was measured using a Horiba NDIR analyzer (MEXA-554JU) and a Cambustion 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%.

Tests were performed with 5 ethanol-gasoline mixtures comprised of 0, 25, 50, 75 and 100% (by liquid volume) of ethanol. The engine was run at stoichiometric condition and MBT ignition timing. The coolant temperature was controlled to 80±2°C. Whenever an operating condition had changed, care was taken to ensure that the engine was in a steady state before exhaust gas was sampled. When the ethanol content was varied in the fuel mixture, the energy content and combustion phasing changed, so did the work output. To get a fair comparison amongst different fuel mixtures, the throttle was adjusted in each test to achieve the same NIMEP within 0.02 bar.

To investigate the effect of engine speed and loads on emissions, the engine test conditions are shown in Table 5.

Table 5. Engine test conditions

NIMEP \ Speed	1500 rpm	2500 rpm
1.5 bar	▓▓▓	
3.8 bar	▓▓▓	
7.5 bar	▓▓▓	▓▓▓

RESULTS AND DICUSSION

TOTAL ORGANIC GAS EMISSIONS – Organic gas emission measurements using the 3 different instruments were compared. The results at medium load, 1500 rpm are shown in Figure 3. To get a fair comparison, the NDIR readings have been adjusted to a wet basis. With pure gasoline the GC and fast FID measurements agreed to within 10%. The difference could be due to experimental errors, different response constants used in calibration and sample loss in the GC sampling system. The GC analysis was able to use different response constants for different species, but the fast FID had to use propane's response factor for all hydrocarbons. This difference alone can give errors up to 10%. A detailed sample loss study was conducted for the GC. The results showed insignificant sample loss except for the C10-C12 species, which had approximately 10% losses. Typically C10-C12 species make up less than 5% of total hydrocarbons. Therefore, the effect of sample loss is insignificant. The NDIR readings were half the FID readings. This finding is well established: the matching IR filter in the Horiba NDIR analyzer was calibrated to n-hexane so overlap of infra-

red absorption bands with other hydrocarbon species was incomplete.
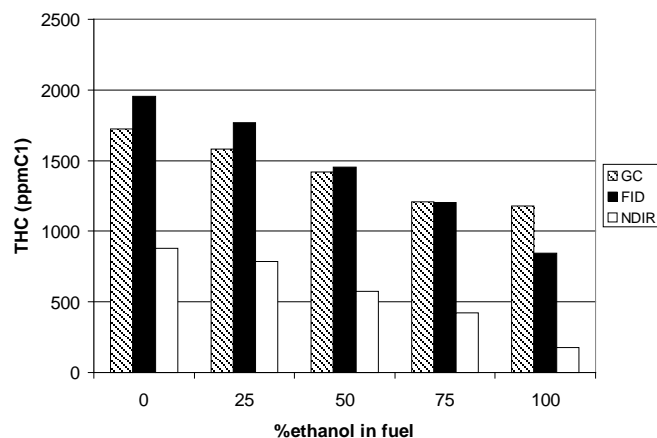

Figure 3. Comparison of 3 total hydrocarbon measurements with different ethanol-gasoline mixtures. 1500 rpm, 3.8 bar NIMEP

As the volume fraction of ethanol increases in the fuel, the fast FID tended to underestimate the organic gas emissions. This observation was a result of that oxygenates had become major components in the exhaust (see the Speciation section below).

SPECIATION – Exhaust gas components were analyzed with the GC according to the method described previously. The calibration run using the gas standard is shown in Figure 4. There are 23 peaks in this chromatograph which corresponds to the 23 gases in the standard. The peaks are very sharp (peak width is about 0.04 min). No extra peaks are present which suggests that the sample is free from contamination in the GC system. The baseline is free of noise. As the oven temperature increases, the baseline only drifts upwards a little. The stability of the baseline helps to ensure that integration of each peak is as accurate as possible. Also, it helps to detect trace components in the exhaust gas.
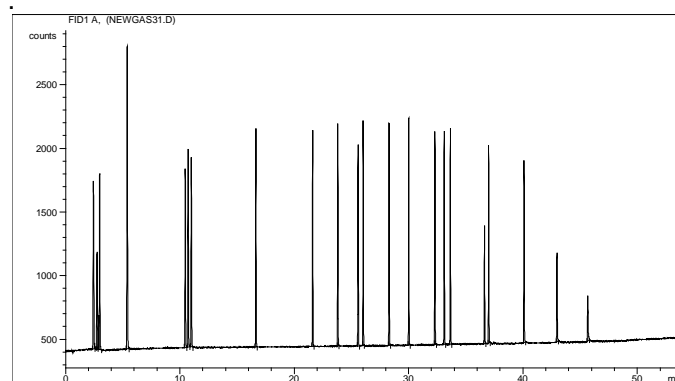

Figure 4. Gas chromatogram of a calibration run. All the 23 components in the gas standard are separated

The exhaust gas chromatogram (Figure 5) contains many more peaks. The baseline appears to be noisy, but in fact it is made up of many small peaks. The number of significant species is the highest (85) when pure gasoline is used. It decreases with increased ethanol content in the fuel. When pure ethanol (E100) is used, only 10 species are identified. On the average, 80% of the peaks are identifiable. These peaks accounts for 93-99% of the total mass.
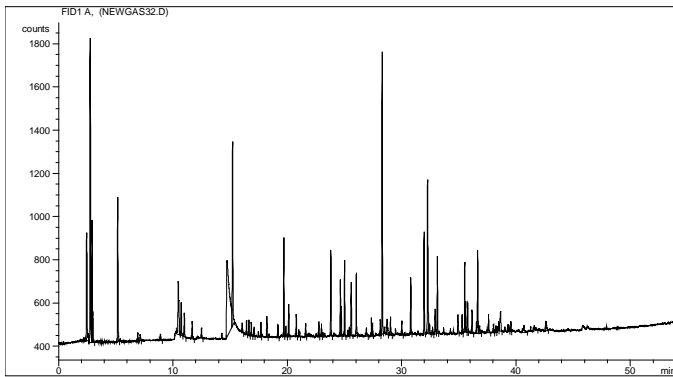

Figure 5. Typical gas chromatogram of exhaust gas. The test conditions were E50, 1500 rpm, 3.8 bar NIMEP

The mole fraction of total organic gas moles for the main species is illustrated in five pie charts (Figures 6–10). Each chart represents one fuel. Those species with at least 3% mole fraction are individually identified. Those below 3% are grouped as 'Others'. All results were obtained at 1500 rpm, 3.8 bar NIMEP. With pure gasoline, the main species are made up of partial reaction products, e.g. methane, ethylene and propene, and fuel species such as toluene and xylene. However there are many trace species (individual mole fraction <3%) which make up 40% of the total moles of organic gas.
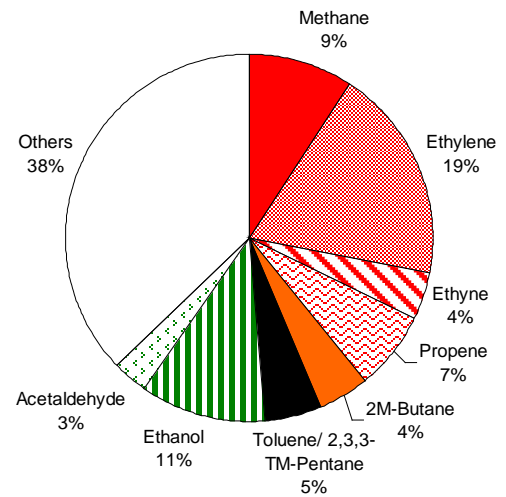

Figure 6. Exhaust species breakdown (as mole fraction of total organic gas moles) with UTG91 gasoline (E0)

Figure 7. Exhaust species breakdown (as mole fraction of total organic gas moles) with E25
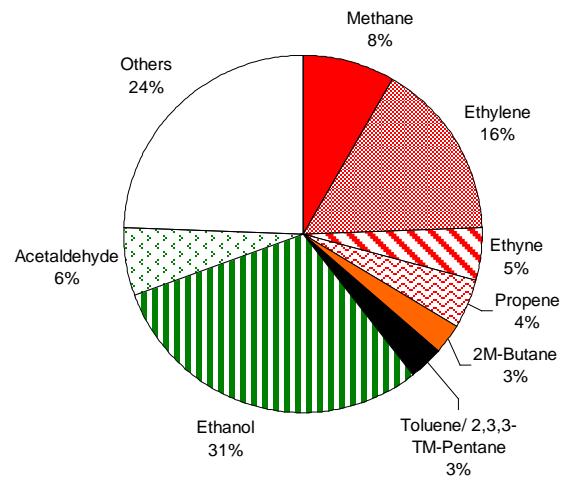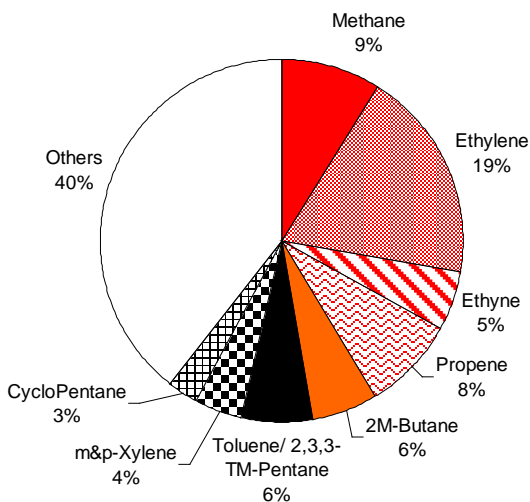

Figure 8. Exhaust species breakdown (as mole fraction of total organic gas moles) with E50
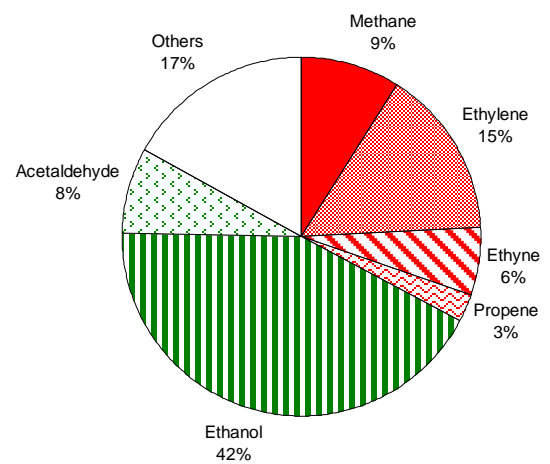

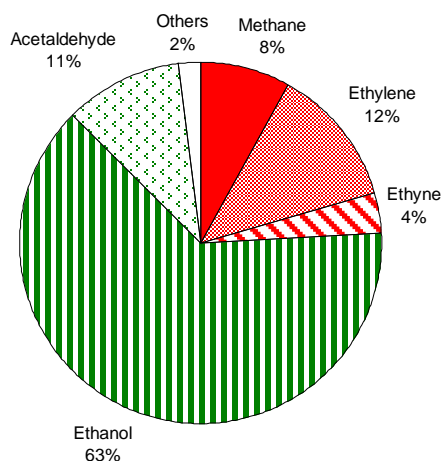**Figure 9. Exhaust species breakdown (as mole fraction of total organic gas moles) with E75**

Figure 10. Exhaust species breakdown (as mole fraction of total organic gas moles) with E100

As ethanol is added to the fuel, oxygenates are found in the exhaust. Two oxygenates have been identified: ethanol and acetaldehyde. The molar ratio of ethanol to acetaldehyde is approximately 5 to 1. Formaldehyde could also exist in the exhaust gas. Since it has no FID response, it was not measured in this study. The higher the ethanol content in the fuel, the higher the mole fraction of oxygenates. For instance, E25 has 14% oxygenates in the exhaust, which increases to 50% with E75, and to 74% with pure ethanol. In contrast the aromatic proportion decreases with increasing ethanol content in the fuel. Lastly, the proportion of partial reaction products, which are mainly C1-C3 hydrocarbons, is roughly one-third regardless what kind of fuel mixtures were used.

FUEL AND EXHAUST FRACTION –. Ethanol due to its fuel-bound oxygen may assist the hydrocarbon oxidation process. An important question arises — Is the reduction in aromatics in the exhaust caused by fuel replacement or by fuel chemistry? Figure 11 may offer an answer. It plots the liquid volume of aromatics and the mole fraction of aromatics against fuel types. As the ethanol content of the fuel increases, the aromatics volume decreases proportionally. The aromatics mole fraction of the exhaust decreases linearly too. If ethanol was able to oxidize aromatics in combustion, the aromatics in the exhaust should decrease more than in proportion. Therefore, a higher ethanol content fuel produces fewer aromatics emission because there is simply less aromatics in the fuel.

Similar behavior is observed in ethanol (see Figure 12). Exhaust ethanol fraction does not increase to 100% as partial reaction products are always present in the exhaust. A major source of hydrocarbon emissions in a SI engine is unburned fuel trapped in crevices found in places such as between the piston, piston rings and cylinder wall. The smaller the fuel component, the less it will be trapped in crevices, hence the amount found in

the exhaust will be less. Given that the aromatics and ethanol emissions change in proportion to the corresponding fuel liquid volume, it is likely that they are trapped in crevices and left unburned.
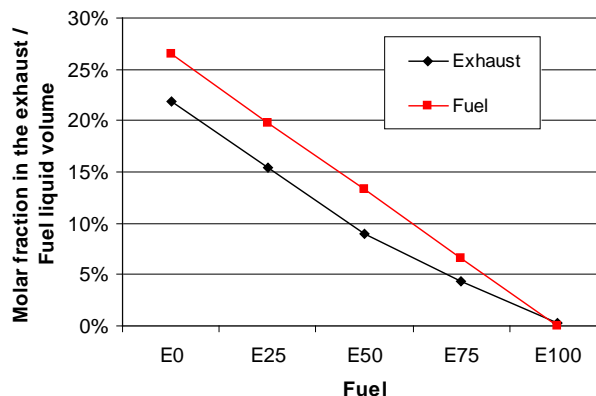

Figure 11. Mole fraction of aromatics in the exhaust and volume fraction as a function of ethanol content in the fuel
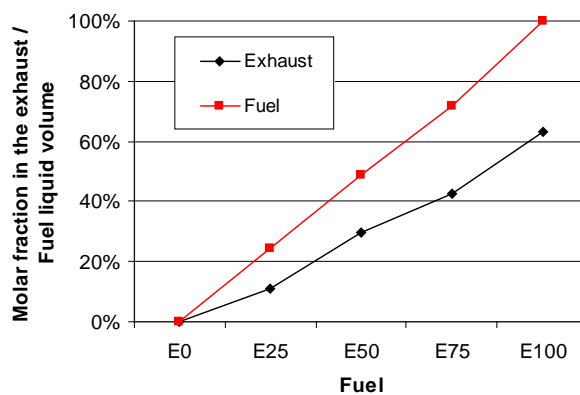

Figure 12. Mole fraction of main species in the exhaust when the engine is fueled with ethanol (E100)

EFFECT OF ENGINE LOAD AND SPEED ON OXYGENATES EMISSIONS – This section investigates how oxygenates emissions are affected by engine load and speed. These results can help develop a correction equation for FID response. The mole fraction of oxygenates in exhaust vs. volume fraction of ethanol in fuel at various engine load is plotted in Figure 13. All the graphs increase linearly. The medium and high-load cases have similar slopes, but the low-load case has a lower slope. This means that at low engine load and using a given fuel, the engine emits the lowest oxygenate fraction. Different engine speeds yield similar results (Figure 14). The increase in oxygenate mole fraction is proportional to the ethanol volume fraction in the fuel. At higher engine speed, the rate of increase is lower.

On the whole, a linear relationship has been observed between the oxygenate mole fraction and ethanol volume fraction in fuel. The effect of engine speed and load only changes the slope. In principle, % oxygenate can be predicted as a function of ethanol content in the fuel, engine speed and load, but this scheme would have limited application because the output is on a mole basis, whilst most hydrocarbon measurements are expressed in ppmC1. To convert the mole fraction to % over total ppmC1 requires a knowledge of each species in the exhaust. Alternatively, the results in Figure 13 and Figure 14 are converted into % of total ppmC1 and collectively plotted in Figure 15. The data points, which are made up of 27 operating points, seem to collapse to form a curve. There are more scatters around the best fit line with E75 and E100, but the error is within 10 percentage points. If this level of error is acceptable, the FID response can be easily corrected since only one equation is required to predict the % oxygenate in the exhaust. The next section will use the result from this graph to derive and validate a FID correction equation.

FID RESPONSE CORRECTION – Firstly this section will derive the FID correction equation based on an empirical correlation. Secondly the correction equation will be validated by comparing the corrected FID readings with the GC readings.

Let the total oxygenate fraction (as C1) in hydrocarbon be z. From the best fit line shown in Figure 15,

$$z = 0.443e^2 + 0.349e \tag{6}$$

where e is the volume fraction of ethanol in fuel.

For oxygenate species i (as C1) in hydrocarbon with a response factor z_i, the corrected FID response is given by

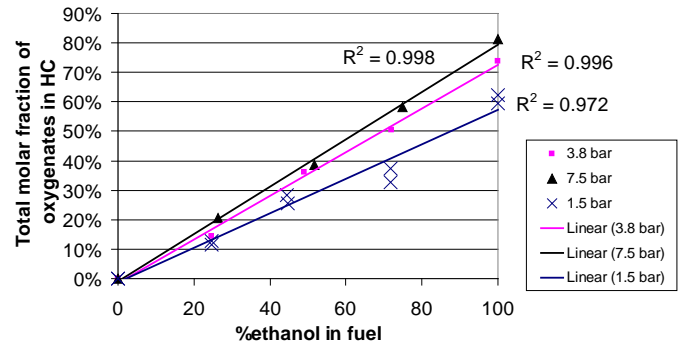$$FID_{corrected} = \frac{FID}{1 - \sum (1 - \alpha_i) z_i} \tag{7}$$

Figure 13. Effect of engine load on oxygenate in exhaust. All results were obtained at 1500 rpm engine speed
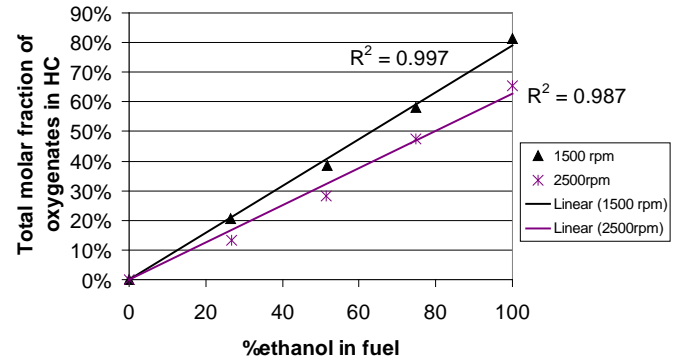

Figure 14. Effect of engine speed on oxygenate in exhaust. The engine was at 7.5 bar NIMEP
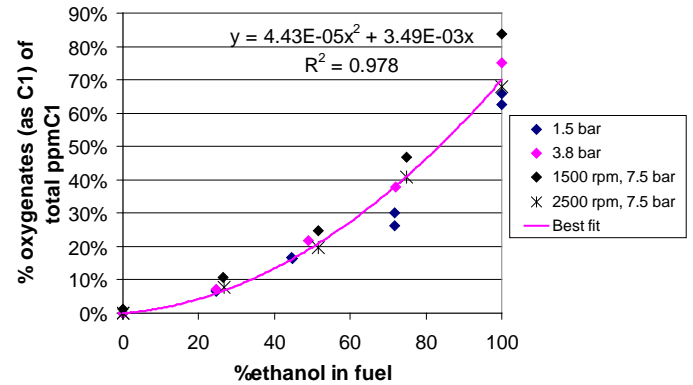

Figure 15. Percentage of oxygenate of total ppmC1 as a function of volume fraction of ethanol in fuel

Since the two major oxygenates species identified are ethanol and acetaldehyde, and their response factors are taken to be the same, i.e. $\alpha = 0.74$, Eq. (7) can be simplified to

$$FID_{corrected} = \frac{FID}{1 - (1 - \alpha) \sum z_i} \tag{8}$$

$\sum z_i$ in Eq. (8) is simply the total oxygenate fraction as total ppmC1. A numerical example can help illustrate the usage of this correction equation. If a FID analyzer returns a reading of 2318 ppmC1 when the engine is running E50, then

$$e = 0.5$$
$$\sum z_i = 0.443 \times 0.5^2 + 0.349 \times 0.5 \qquad (9)$$
$$= 0.285$$

Substituting the results from Eq. (9) into Eq. (8) gives

$$FID_{corrected} = \frac{2318}{1 - (1 - 0.74) \times 0.285} \qquad (10)$$
$$= 2504 \text{ ppmC1}$$

The correcting equation is applied to the FID readings. They can be readily compared with the GC readings, which have correctly accounted for the reduced FID response of oxygenates. Any differences between these two values will show the error in using the correction equation. Figures 16–18 show such comparisons at different loads and speeds. The oxygenate fraction $\sum z_i$ is estimated from an empirical correlation (Eq. (6)), which is not 100% accurate. Moreover experimental errors such as drift in FID calibration will prevent the GC and FID corrected readings to match. Furthermore, the Cambustion FID only uses propane gas for calibration. This implies the response factors for all hydrocarbons are assumed to be the same as propane, which is accurate within 5-10%. Therefore, to differentiate the error which is due to deficiency in the correction equation, or due to other experimental errors, two corrected values are given. The first one uses the true oxygenate fraction (solid bar) to perform the correction. The second one make use of Eq. (6) to calculate the oxygenate fraction (clear bar). The difference between the two bars indicates the error in estimating the oxygenate fraction in the exhaust.

In general, the solid and clear bars are mostly identical. Therefore, it can be concluded that oxygenate fraction can be estimated with negligible error. A bigger difference is found by comparing the solid bar to the GC reading (hatched bar). No patterns can be identified as to which engine conditions or fuels create the greatest error. The main reasons for the difference are summarized below:

- Drift in FID calibration before and after tests (1-2%)
- FID uses a single response factor for all hydrocarbons
- Uncertainty in acetaldehyde FID response factor
- Possible sample loss of heavy hydrocarbons before analysis

Nevertheless, the difference between the corrected FID and GC readings is within 10% on average. Hence a FID reading can be corrected with an accuracy of 90% when ethanol volume fraction in the fuel is known.
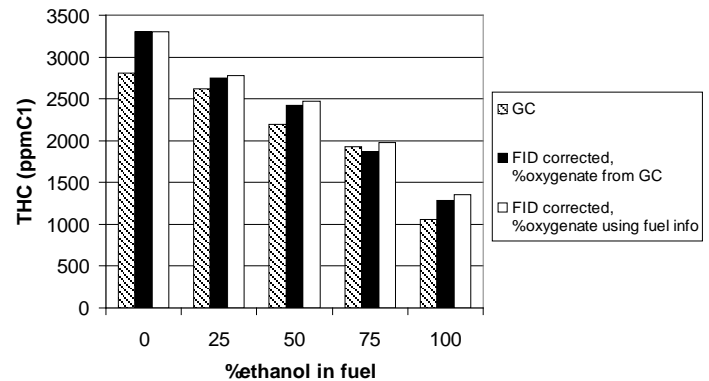

Figure 16. Comparison of GC and FID corrected total hydrocarbon (THC) readings as ppmC1. Operating conditions: 1500 rpm, 1.5 bar NIMEP
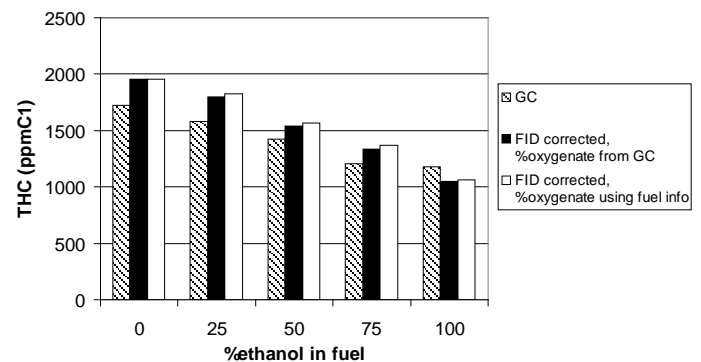

Figure 17. Comparison of GC and FID corrected total hydrocarbon (THC) readings as ppmC1. Operating conditions: 1500 rpm, 3.8 bar NIMEP
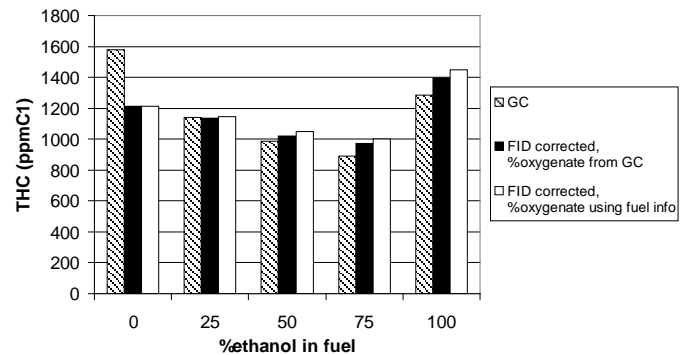

Figure 18. Comparison of GC and FID corrected total hydrocarbon (THC) readings as ppmC1. Operating conditions: 2500 rpm, 7.5 bar NIMEP

CONCLUSION

The gas chromatographic method developed in Auto/Oil program was applied to speciate exhaust gas from a PFI-SI engine running pure gasoline and gasohols. The GC analysis successfully identified over 80% of all hydrocarbons which accounted for 93-99% mass. The main species identified were methane, ethylene, ethyne, propene, 2-methylbutane and toluene. Whenever gasohols were used, ethanol and acetaldehyde were the main species.

It was found that the amount (as mole fraction of total moles) of aromatics and ethanol changed in proportion to the corresponding fuel liquid volume. This finding suggests that ethanol does not promote the oxidation of aromatics, and that aromatics and ethanol exhaust emissions are likely caused by unburned fuel trapped in crevices.

The oxygenate fraction of total hydrocarbons (as ppmC1) was found to be weakly dependent on engine speed and load. This enabled a correction equation compensates for the reduced response of FID to oxygenates to be developed. The correction equation was applied to the FID readings and then validated against the GC readings. Results show that the two readings agreed within 10%. Further analysis reveals that the error is not due to the empirical correlation used in the correction equation. Therefore, a FID hydrocarbon reading taken from a PFI-SI engine running gasohol can be corrected to 90% accuracy.

ACKNOWLEDGMENTS

REFERENCES

1. Cheng, W.K., Summers, T., and Collings N. The Fast-Response Flame Ionization Detector. *Prog. Energy Combust. Sci.* **24**, p. 89–124, 1998.
2. Lipari, F. *Determination of Individual Hydrocarbons in Automobile Exhaust from Gasoline-, Methanol- and Variable-Fueled Vehicles. Journal of Chromatography* **503**, p. 51–68, 1990.
3. Jemma, C.A. Shore, P.R. and Widdicombe, K.A. Analysis of C1-C16 Hydrocarbons Using Dual-Column Capillary GC: Application to Exhaust Emissions from Passenger Car and Motorcycle Engines. *Journal of Chromatographic Science* **33**, p. 34-48, 1995.
4. Jensen, T.E., Siegl, W.O., Richert, J.F.O., Loo, J.F., Prostak, A., Lipari, F., and Sigsby, J.E. Advanced Emission Speciation Methodologies for the Auto/Oil Air Quality Improvement Research Program – I. Hydrocarbons and Ethers. *SAE Technical Paper 920320*, 1992.
5. Siegl, W.O., Richert, J.F.O., Trescott, E.J., Schuetzle, D., Swarin, S.J., Loo, J.F., Prostak, A., Nagy, D., and Schlenker, A.M. Improved Emission Speciation Methodology for Phase II of the Auto/Oil Air Quality Improvement Research Program – Hydrocarbons and Oxygenates. *SAE Technical Paper 930142*, 1993.
6. Rudlein, N., Geiger, W., Pelz, N. and Scherrbacher, H.J. Development of a Single Run Method for the Determination of Individual Hydrocarbons (C2-C12) in Automotive Exhaust by Capillary Gas Chromatography. *SAE Technical Paper 940827*, 1994.
7. Olson, K.L., Sinkevitch, R.M. and Sloane, T.M. Speciation and Quantification of Hydrocarbons in Gasoline Engine Exhaust. *Journal of Chromatographic Science* **30**, p. 500–508, 1992
8. Dec, J.E., Davisson, M.L., Sjoberg, M., Leif, R.N. and Hwang, W. Detailed HCCI Exhaust Speciation and the Sources of Hydrocarbon and Oxygenated Hydrocarbon Emissions. *SAE Technical Paper 2008-01-0053*, 2008.
9. Swarin, S.J., Loo, J.F., Chladek, E. Drouillard, M.S. and Tejada, S.B. Advanced Emissions Speciation Methologies for the Auto/Oil Air Quality Improvement Research Program – II. Aldehydes, Ketones, and Alcohols. *SAE Technical Paper 920321*, 1992.
10. Adachi, M., Yamagishi, Y., Inoue, K. and Ishida, K. Automotive emission analyses using FTIR spectrophotometer. *Journal of Fuels and Lubricants*, **101**, p. 820–827, 1992
11. Loos, M.J. Richert, J.F.O, Mauti, A., Kay, S., Chanko, T., and Shah, S.D. Enabling Flex Fuel Vehicle Emissions Testing – Test Cell Modifications and Data Improvements. *SAE Technical Paper 2009-01-1523*, 2009.
12. Loo, J.F. and Parker, D.T. Evaluation of a Photoacoustic Gas Analyzer for Ethanol Vehicle Emissions Measurement. *SAE Technical Paper 2000-01-0794*, 2000.
13. Chen, K.C. Fuel Effects on Driveability and Hydrocarbon Emissions of Spark-Ignition Engine During Starting and Warm-Up Process. Ph.D. Thesis, Massachusetts Institute of Technology, 1996.
14. Cambustion, Suitability of HFR500 for Ethanol Measurements. Application Note HFR06, Cambustion Ltd. Retrieved May 1, 2009, from http://www.cambustion.co.uk/applications/hfr500/hfr06v01%20ethanol.pdf

CONTACT

Dr. Kenneth Kar, 31-168, MIT, Cambridge, MA 02139; email: kkar@mit.edu

Prof. Wai Cheng, 31-165 MIT, Cambridge, MA 02139;
email: wkcheng@mit.edu

DEFINITIONS, ACRONYMS, ABBREVIATIONS

AQIRP: Auto/Oil Air Quality Research Program

aTDC: after Top Dead Center

bBDC: before Bottom Dead Center

BDC: Bottom Dead Center

bTDC: before Top Dead Center

E*nn*: An ethanol/gasoline mixture containing *nn*% of ethanol by volume

FID: Flame ionization detector

GC: Gas chromatograph

HC: Hydrocarbons

MBT: Minimum ignition advance for best torque

NIMEP: Net indicated mean effective pressure

PFI: port fuel injection

ppmC1: part per million of carbon1, a commonly used unit for hydrocarbon measurements

RI: Retention index

SI: Spark Ignition