

Detailed HCCI Exhaust Speciation and the Sources of Hydrocarbon and Oxygenated Hydrocarbon Emissions

John E. Dec*, M. Lee Davisson[†], Magnus Sjöberg*,
Roald N. Leif[†] and Wontae Hwang*

*Sandia National Laboratories

[†]Lawrence Livermore National Laboratory

ABSTRACT

Detailed exhaust speciation measurements were made on an HCCI engine fueled with iso-octane over a range of fueling rates, and over a range of fuel-stratification levels. Fully premixed fueling was used for the fueling sweep. This sweep extended from a fuel/air equivalence ratio (ϕ) of 0.28, which is sufficiently high to achieve a combustion efficiency of 96%, down to a below-idle fueling rate of $\phi = 0.08$, with a combustion efficiency of only 55%. The stratification sweep was conducted at an idle fueling rate, using an 8-hole GDI injector to vary stratification from well-mixed conditions for an early start of injection (SOI) (40°CA) to highly stratified conditions for an SOI well up the compression stroke (325°CA, 35°bTDC-compression). The engine speed was 1200 rpm.

At each operating condition, exhaust samples were collected and analyzed by GC-FID for the C1 and C2 hydrocarbon (HC) species and by GC-MS for all other species except formaldehyde and acetaldehyde. These two species were analyzed using high-performance liquid chromatography. In addition, standard emissions-bench exhaust analysis equipment was used to measure total HC, CO, CO₂, O₂, and NO_x simultaneously with the sampling for the detailed-speciation analysis. Good overall agreement was found between the emissions-bench data and total HC from the detailed measurements.

Unreacted fuel, iso-octane, was by far the most prevalent HC species at all operating conditions. Numerous other HC and oxygenated HC (OHC) species were found that could be identified as breakdown products of iso-octane. Several smaller HC and OHC species were also identified. At the highest ϕ , emissions of all species were low, except iso-octane. As ϕ was reduced, emissions of all species increased, but the rate of increase varied substantially for the different species. Analysis showed that these differences were related to the degree of breakdown from the parent fuel and the in-cylinder location where they formed. SOI-sweep results indicated that stratification improves combustion efficiency by reducing the fuel penetration to the crevice and cylinder-wall boundary-layer regions, as well as by creating a locally richer mixture that burns hotter and more completely.

INTRODUCTION

Homogeneous charge compression ignition (HCCI) engines are being widely investigated because they can provide both high diesel-like efficiencies and ultra-low nitrogen oxide (NO_x) and particulate emissions. However, 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 hydrocarbons (HC), oxygenated hydrocarbons (OHC), and carbon-monoxide (CO) [1-4]. These emissions become particularly high at low loads, with a commensurate drop in the combustion efficiency to unacceptably low levels [3-5]. Research has shown that mixture stratification can increase low-load combustion efficiency substantially [3,6], and in a recent work, the authors showed that improved stratification could produce combustion efficiencies at idle that were only a few percent less than those for high loads [7]. Despite these improvements, however, aftertreatment will almost certainly still be required at all loads to control these HC, OHC, and CO emissions.

Although HC emissions have been measured since the early investigations of HCCI combustion [1,2], information on the individual species comprising these emissions is scant. This is because HC emissions are typically measured with an exhaust analyzer that measures the total carbon in the exhaust HC, but gives no information on species composition. Moreover, these HC analyzers use a flame ionization detector (FID), which is not sensitive to carbon atoms that are bound to oxygen. Therefore, OHC compounds give a reduced signal, or give no signal at all for species like formaldehyde, which have only one carbon atom that is bound to an oxygen atom. As a result, the presence of OHC compounds was not noted until more recently [8-10].

Before discussing the behavior of individual HC and OHC species, it is important to understand the primary sources of HC and OHC emissions and how their amounts are affected by operating condition. Figure 1 shows the trends of combustion efficiency and emissions plotted as a function of fuel/air equivalence ratio (ϕ) for operation with a fully premixed intake mixture of iso-

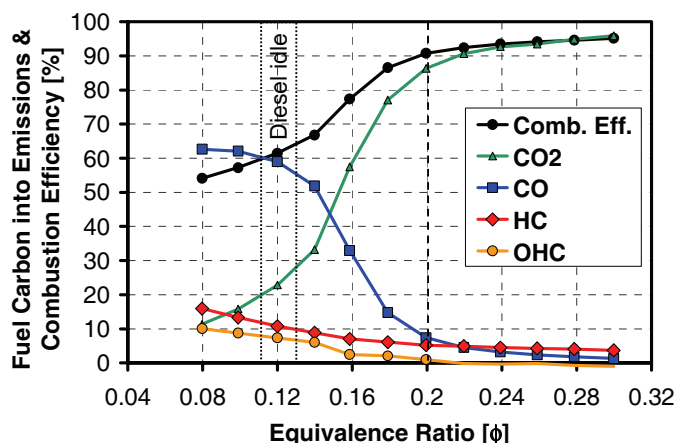


Figure 1. Exhaust emissions as function of fueling rate for fully pre-mixed fueling for iso-octane, CA50 = TDC, 1200 rpm, from Ref. [11].

octane and air, at a compression ratio (CR) of 18 (reproduced from Ref. [11]). The emissions are given as the percentage of total fuel carbon in each of the exhaust species to remove changes due solely to the quantity of fuel supplied. The 50% burn point (CA50) was held constant at top dead center (TDC). At intermediate loads, where ϕ is above 0.2 (right of the dashed line in Fig. 1), CO and HC levels are low, and carbon dioxide (CO₂) levels are high, resulting in high combustion efficiencies, on the order of 95%. As discussed in previous works [3,12-14], the small combustion inefficiencies at these higher loads are thought to result primarily from unburned or partially reacted fuel in the crevices or near-wall regions. However, when ϕ is decreased below 0.2 (to the left of the dashed line), CO levels start to rise rapidly, and HC and OHC also begin to increase, while CO₂ levels sharply decrease. As a result, combustion efficiency drops, reaching unacceptable levels of about 60% at diesel idling conditions ($0.11 \leq \phi \leq 0.13$). At these low loads, the mixtures are so dilute that combustion temperatures are too low for the bulk-gas reactions to go to completion before they are quenched by the expansion stroke [3-5,8,14,15]. Previous works have generally focused on the bulk-gas CO-to-CO₂ reactions becoming incomplete (causing the high CO emissions) as peak combustion temperatures are reduced below about 1500 K [3,5,8]. However, when temperatures become sufficiently low (*i.e.*, well below 1500 K), the first steps of fuel oxidation or even the fuel breakdown reactions become too slow to go to completion [3,8]. Thus, the in-cylinder locations where HC and OHC emissions form vary with fueling rate.

As discussed above, typical exhaust-gas analyzers are less sensitive to OHC compounds, so a direct measurement of total OHC emissions is not easily obtained. However, it was noted that closing the carbon balance between the exhaust species and the supplied fuel showed an increasing amount of carbon unaccounted for as ϕ was reduced below 0.2 [3]. The trend in the quantity of this “missing” carbon is generally the same as that expected for the amount of OHC emissions based on single-zone modeling results [3,8]. Therefore, this error in

carbon-balance closure is shown as OHC emissions in Fig. 1, as discussed more completely in Ref. [3]. Clearly, this is not an accurate measurement of the total OHC since it includes the accumulated errors from all the measurements (CO, CO₂, and HC). For example, the data in Fig. 1 show non-physical, slightly negative OHC values for $0.22 \leq \phi \leq 0.3$, as a result of small errors in the other measurements. Nevertheless, this carbon-closure measurement gives an indication of the expected trends in OHC.

Because of the difficulty in measuring OHC species, their presence in HCCI exhaust was not noted until 2002, when they were reported independently in three separate studies [8-10] and later verified in a fourth study [16]. These previous studies also provided some information on the individual OHC and HC species, as follows:

- Dec [8] presented single-zone computational results showing that significant concentrations of OHC compounds should be present in HCCI exhaust at low loads, and that the amount of OHC should increase with reduced fueling, as bulk-gas combustion becomes less complete. In a subsequent paper, Dec and Sjöberg [3] identified the most prevalent of these species as formic acid, formaldehyde, acetaldehyde, and acetaldehyde, based on computational results for iso-octane, using the detailed mechanism from LLNL [17]. They also noted that the computations predicted methane to be the most prevalent HC species from the bulk gas at low loads.
- Kaiser *et al.* [9] presented experimental exhaust speciation data from a gasoline-fueled HCCI engine obtained using gas-chromatography combined with a FID or a mass spectrometer (GC-FID and GC-MS). They identified three OHC species: formaldehyde, acetaldehyde and benzaldehyde, and showed that the percent of fuel carbon in these species increased as fueling was reduced. In a follow-on work, Kaiser *et al.* [18] presented emissions data in tabular form for a large number of HC and OHC species for gasoline-fueled HCCI. They also plotted the trends of a few species, showing that the percent of fuel carbon in these species increases with decreased fueling.
- Iida *et al.* [10] used Fourier transform infra-red (FTIR) analysis to perform a limited exhaust speciation analysis for an HCCI engine fueled with *n*-butane. They found significant quantities of the OHC species formaldehyde and acetaldehyde. They also identified four HC species, with the most prevalent being unreacted fuel (*n*-butane), followed by ethene, methane, and propene. They also show a general trend of the concentration of all species increasing with reduced fueling.
- Later, Lemel *et al.* [16] also presented data confirming the presence of formaldehyde using FTIR analysis. In agreement with the other studies, they showed that its concentration increased with reduced fueling. This study also investigated the effect of fuel type, showing that formaldehyde concentrations were higher for two-stage-ignition fuels.

These previous investigations have added considerably to our understanding of HC and OHC emissions; however, there are many aspects that are still not well understood.

The objective of the current work is to obtain high-quality HC and OHC exhaust speciation data over a range of operating conditions, and to analyze these data to better understand the in-cylinder processes and sources of these emissions. To accomplish this, accurate HC and OHC species sampling and analysis techniques were developed. Then, using these techniques, data were acquired for two parametric sweeps in an HCCI engine. First, for premixed fueling, the fueling rate was varied incrementally from a mid-range load down to below-idle conditions. Second, since fuel/air mixture stratification can greatly improve low-load combustion efficiency [3,6,7], a gasoline-type direct injector (GDI) was used to systematically delay the start of injection (SOI) to vary the mixture formation from well-mixed to highly stratified conditions at an idle fueling rate of $\phi = 0.12$. The fuel selected for these studies was iso-octane, which is a good surrogate for gasoline in terms of engine operation [4]. However, unlike gasoline, this single-component fuel allows the species resulting from fuel breakdown to be easily understood and tracked. As fueling rate and mixture stratification are varied, the data show distinctly different trends for the various HC and OHC species. Analyzing these trends in terms of the expected progress of fuel breakdown and oxidation provides an improved understanding of the in-cylinder processes of HCCI combustion and emissions formation for both well-mixed and mixture-stratified operation.

In addition, using iso-octane as the fuel provides a database for comparison with single-zone, multi-zone, and full CFD models that use iso-octane chemical-kinetic mechanisms, as demonstrated in a concurrent paper [19]. Finally, this database of HC and OHC emissions will be helpful for the development of oxidation catalysts with appropriate low-temperature light-off characteristics, which will likely be needed to control these emissions from HCCI engines.

A description of the HCCI research engine facility and conventional data acquisition methods are given in the next section. This is followed by a description of the sampling and analysis techniques used for the detailed speciation of the HC and OHC emissions. Then, the results are presented in two parts corresponding to the equivalence-ratio and fuel-stratification sweeps. In the final section, the findings are summarized and conclusions are drawn.

EXPERIMENTAL SETUP

ENGINE FACILITY

The HCCI research engine used for this study was derived from a Cummins B-series medium-duty, six-cylinder diesel engine, which is a typical medium-duty diesel engine with a displacement of 0.98 liters/cylinder. Figure 2a shows a schematic of the engine, which has

been converted for single-cylinder operation. The engine specifications and operating conditions are listed in Table 1. A complete description of the engine and facility may be found in Ref. [3].

The engine was equipped with a custom HCCI piston as shown in Fig. 2b. This combustion chamber design was chosen because it provided a large squish clearance and a minimum top ring-land crevice volume that amounts to only 2.1% of the top dead center (TDC) volume (including the volume behind the top piston ring) for the 14:1 compression-ratio piston used in this study.¹ Most of our previous low-load HCCI studies with iso-octane and gasoline fueling, including the data presented in Fig. 1, used a CR = 18 piston with naturally aspirated intake conditions [3-5,11]. However, a CR = 14 piston was installed in the engine for other concurrent studies, so we maintained this CR = 14 for the current investigation. With CR = 14 and an intake pressure (P_{in}) of 100 kPa, the intake heating system (which was limited to approximately 230°C) was not sufficient for low-load combustion of iso-octane. Therefore, the intake pressure was boosted to 135 kPa, so the TDC pressure with CR = 14 matched that with CR = 18 and $P_{in} = 100$ kPa. The intake temperature (T_{in}) was also increased to match the TDC temperature of the CR = 18 cases, and was adjusted as necessary to maintain the 50% burn point at TDC. This required $180^{\circ}\text{C} \leq T_{in} \leq 210^{\circ}\text{C}$ for intake equivalence ratios from 0.28 to 0.08, respectively. With these adjustments, the combustion efficiency, CO, and HC levels for the CR = 14 data were nearly identical to the older CR = 18 data, as shown in Ref. [7].² There were small differences in the CO₂ levels, mainly as the result of a new CO₂ analyzer. This difference also produced a difference in the estimated OHC values deduced from the carbon closure, as will be shown later. The effects of fuel stratification on overall emissions and combustion efficiency were also quite similar for the two compression ratios [7].

The engine was equipped with two fueling systems. For the equivalence-ratio sweep, fueling was accomplished with a fully pre-mixed fueling system using an electrically heated fuel vaporizer, as shown near the top of Fig. 2a. For the investigation of mixture-stratified operation, fuel was supplied by an 8-hole GDI injector mounted in the center of the cylinder head. The sprays from this injector had a 70° included angle (Fig. 2c). In order to accurately determine the amount of fuel supplied, a positive-displacement flow meter was installed on the common fuel line that supplies either the injector in the engine or the injector in the vaporizer. The meter was calibrated by mass at multiple flow rates, using the same fuel-supply system used for engine operation. All injection timings given are the actual start of injection. The injec-

¹ It should be noted that the valve pocket and head gasket crevices, which are not shown in Fig. 2b, contribute to the TDC volume, making the actual CR = 14.

² Although the differences in intake conditions and CR cause the pressure and temperature histories to be different for the two data sets, the differences are very small near TDC, and thus appear to have little effect on these data for which CA50 = TDC, and the 10-90% burn duration is only 3.5 – 11°CA.

TABLE 1. Engine Specifications and Operating Conditions

Displacement (single-cylinder).....	0.981 liters
Bore	102 mm
Stroke	120 mm
Connecting Rod Length	192 mm
Geometric Compression Ratio	14:1
No. of Valves	4
IVO	0°CA*
IVC	202°CA*
EVO	482°CA*
EVC	8°CA*
Swirl Ratio	0.9
Injector Type	8-hole, GDI
Injector Spray (included angle)	70°
Injection Pressure	120 bar
Engine Speed	1200 rpm
Intake Pressure	135 kPa (abs.)
Coolant Temperature	100°C
Fuel	Iso-Octane

* 0°CA is taken to be TDC intake. The same camshaft is used as in previous studies, but the valve-event timings have been slightly adjusted to better represent the point of 0.1 mm lift.

tion duration was 0.63 ms (4.5°CA) at the fueling rate used for the SOI sweep ($\phi = 0.12$).

The intake air was supplied by an air compressor and electrically heated to the desired intake temperature. An auxiliary heater located close to the engine (see Fig. 2a)

precisely controlled the intake temperature so the combustion phasing could be maintained with 0.2° crank angle (CA) of the desired value. The air flow was metered and controlled by a sonic-nozzle orifice.

Prior to running, the engine was preheated to 100°C by electrical heaters on the “cooling” water and lubricating oil circulation systems, and this temperature was held steady during the experiments. At each operating point, the engine was allowed to run for several minutes until all measured parameters were stable, at which point the data were acquired.

Iso-octane was the fuel used for this study, as discussed in the Introduction. All data were taken at an engine speed of 1200 rpm, with the intake air flow adjusted to maintain $P_{in} = 135$ kPa (absolute). No exhaust-gas recirculation was used.

CONVENTIONAL DATA ACQUISITION

Cylinder pressure measurements were made with a piezoelectric transducer (AVL QC33C) at ¼°CA increments. The measurements were pegged (adjusted to match) to the intake pressure near bottom dead center (BDC) where the cylinder pressure reading was virtually constant for several degrees. For all data presented, 0°CA is defined as TDC at the start of the intake stroke (so TDC compression is at 360°). This eliminates the need to use negative crank angles or combined BTDC, ATDC notation.

For all experiments, the combustion phasing was controlled so that the 50% burn point (CA50) was maintained

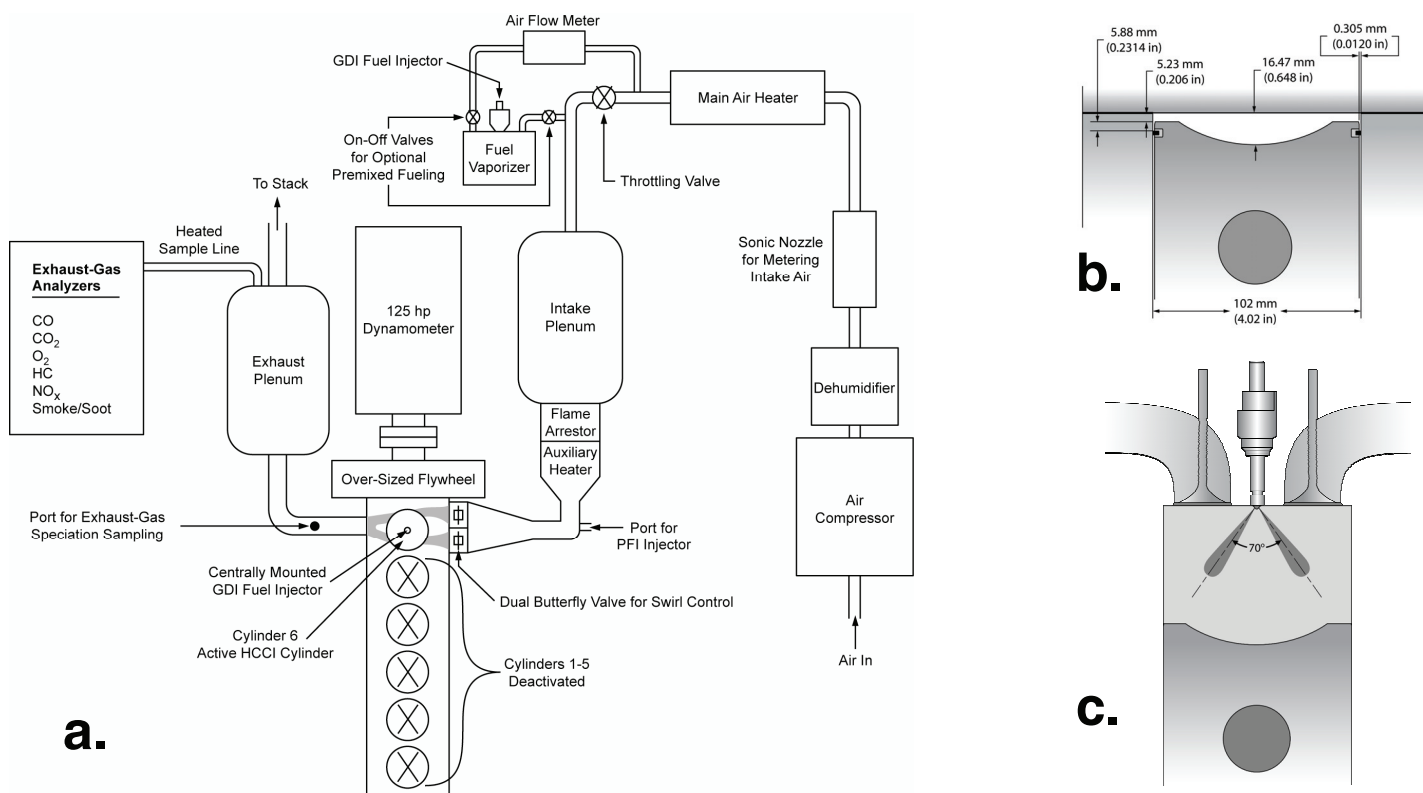


Figure 2. Schematics showing: a) the HCCI engine facility, b) combustion chamber dimensions at TDC, and c) the layout and spray angle of the 8-hole GDI fuel injector, with the piston at the 280°CA position.

at TDC (360°C). CA50 was determined from the cumulative apparent heat-release rate (AHRR), computed from the cylinder-pressure data (after applying a 2.5 kHz low-pass filter [3]). Computations were performed for each individual cycle, disregarding heat-transfer and assuming a constant ratio of specific heats [20]. The average of 100 consecutive individual-cycle CA50 values was then set to TDC by adjusting the intake temperature.

Conventional exhaust emissions data were also acquired, with the sample being drawn from the exhaust plenum using a heated sample line (see Fig. 2a). CO, CO₂, HC, NO_x, and O₂ levels were measured using standard exhaust-gas analysis equipment as listed in Table 2. Smoke measurements were made with an automated smoke meter, but levels were zero or near-zero for all conditions studied and are not reported.

Table 2. Emissions-Bench Analysis Equipment

CO	Non-Dispersive Infrared Detector, Rosemount 880A
CO ₂	Non-Dispersive Infrared Detector, California Analytical Instruments 602
HC	Flame Ionization Detector (FID), Rosemount 400A
NO _x	Chemiluminescence Analyzer, Rosemount 951A
O ₂	Paramagnetic Analyzer, Rosemount 755R
Smoke	Optical-Density of Filter Paper, AVL415S

DETAILED HC AND OHC SPECIATION SAMPLING AND ANALYSIS

SAMPLING

Exhaust samples for detailed speciation were collected in Tedlar gas sampling bags. Bags were prepared by three successive evacuations and purgings with dry nitrogen. A separate sample was collected for formaldehyde and acetaldehyde using a dinitrophenylhydrazine (DNPH) derivatizing solution as described by Lipari and Swarin [21]. The solution was prepared by dissolving 500 mg reagent grade DNPH in 2-normal hydrochloric acid under a dry nitrogen atmosphere. A new batch of DNPH solution was prepared before each experiment.

All samples were drawn from a small port on the exhaust runner located between the cylinder head and the exhaust plenum (Fig. 2a). Fitted to the port was a valve that provided the option to direct flow into two different 1/8 inch Teflon tube sampling lines wrapped in heating tape. One line led to a small pump that filled a 500 ml or one-liter Tedlar bag at 2 liters per minute. Two separate bag samples were collected, one for the C1-C2 hydrocarbons, and the other bag for the remaining species. The other line was attached to two 25 ml Pyrex sparge tube vessels connected in series with Teflon fittings. The vessels were filled with DNPH solution. Exhaust was pulled through the DNPH solution at 100 cubic centimeters per minute using a small pump whose rate was controlled by a small needle valve upstream of the sparge tubes. Optimal flow rates were determined in the lab by pulling formaldehyde and acetaldehyde standards from a

Tedlar bag. Collection efficiency of these standards was ~100%, measured by the recovery of the derivatized aldehydes. During exhaust sample collection, average flow rates and collection times were recorded using an electronic flow meter. Sampling times ranged from 3 – 20 minutes depending on anticipated concentrations. Excessive sample times resulted in a light precipitate forming in the DNPH solution. The DNPH solution was maintained at room temperature during sampling. Immediately after sampling it was transferred to an amber-colored glass bottle and sealed with a Teflon-lined cap.

ANALYSIS

The C1-C2 hydrocarbons were analyzed using an SRI 8610C gas chromatograph equipped with a flame ionization detector. Samples were introduced using an electronically actuated VICI/Valco multiport gas sampling valve with a 1.0 ml sample loop, with direct injection into a 6 ft x 1/8 inch stainless steel silica gel packed column, using helium as the carrier gas. Fixed gas standards were purchased from Supelco and used for calibration.

All other hydrocarbons and oxygenated hydrocarbons were analyzed using an HP5890/5972MSD gas chromatograph mass spectrometer (GC-MS) within one week of collection. A Tedlar bag sample and a 25 ml gas-tight syringe were first heated in an oven to 60°C. A 25 ml aliquot was drawn into the syringe and subsequently injected directly into a heated glass tube purged with a 25 cc/min high-purity helium flow. The helium swept the sample onto an adsorbent comprised of a mixture of Carbopak B and carboxen (Supelco VOCARB 3000). After 20 minutes the trap was heated to 250°C and the adsorbed species were concentrated onto the head of the GC column using the helium flow. Compound separation was facilitated using a DB-502 capillary column heated from 35°C to 250°C at 5°C/min and held for 10 minutes. Injector and detector temperatures were held at 225°C and 250°C, respectively. Standards were prepared by injecting 1-5 microliters of authentic standards into a Tedlar bag filled with dry nitrogen and analyzed using the same method.

For quantitative analysis, the standard preparations were injected at three different concentrations and total ion currents (TICs) were integrated for linear regression analysis. For most species detected and identified in the exhaust samples, the TICs were sufficient for producing concentrations that were consistent with anticipated levels implicit in the standard exhaust-gas analysis equipment. However, some species required quantification using specific ion fragments, since several showed significant overlap with a broad water peak or a co-eluting species. Eleven different authentic standards were used in total, some of which were the same as those detected in exhaust samples, but others were chosen for their similarity to a large number of exhaust species in order to simplify the quantitative analysis. With the exception of formaldehyde, response factors varied by approximately a factor of two among hydrocarbon standards, and a factor of seven for oxygenated hydrocarbons. Standards with similar structures to exhaust species

were routinely matched for quantification when an authentic (*i.e.* exactly matching) standard was not available.

DNPH samples were processed in duplicate by aliquoting 200 microliters of solution into a 10 ml vial and adding 2 ml of hexane (95% n-hexane purity). The vial was sealed and shaken for one minute and the immiscible phases were allowed to separate. Then the hexane layer was pipetted into a glass centrifuge tube and dried at <50°C under a gentle stream of dry nitrogen. The dried residue was re-dissolved in acetonitrile. Authentic formaldehyde and acetaldehyde standards were also derivatized and extracted to determine the method recovery efficiencies, which were 55±5% and 77±5% for formaldehyde and acetaldehyde, respectively. For low concentrations, the sample was extracted a second time with hexane, and recovery efficiency was >80%. Results from routine duplicate extractions were typically in agreement to ≤10%. After extraction, samples were measured for derivatized products using a ThermoFinnigan Survey high-performance liquid chromatograph (HPLC). Compound separation was facilitated by a C18 stationary phase and gradient elution starting with a 5% acetonitrile/95% water mobile phase and ending with 20% acetonitrile/80% water over 24 minutes of analysis time. Multiple wavelength photodiode array detection of compounds was initially used to identify formaldehyde and acetaldehyde derivatives, but a wavelength of 360 nm was routinely used in calibration.

Comparison of the GC-MS and DNPH HPLC methods is useful for understanding analytical errors over various concentration levels. For example, the formaldehyde results suggest that the two methods produce similar results to within 20% of each other (Table 3). However, the results using the DNPH HPLC method are considered here as more representative of actual concentrations because we had better experimental controls, better agreement with measurements using the standard emissions-bench exhaust-gas analysis equipment, and smoother trends over the two parametric sweeps. Consequently, GC-MS appears to over-represent the concentration at lower levels, whereas it under-represents at high levels. The latter is likely due to losses during sample storage and introduction into the instrument before analysis, whereas the former reflects limits to preparation and analysis of low concentration standards. The HPLC values are used for all of the data presented in the Results section.

Table 3. Comparison of formaldehyde results between GC/MS and DNPH HPLC methods for the ϕ -sweep experiment.

ϕ	ppm CH ₂ O (GC-MS)	ppm CH ₂ O (DNPH HPLC)	Difference
0.28	17.6	14.8	2.8
0.24	26.9	15.7	11.2
0.20	25.1	20.9	4.2
0.16	40.3	46.1	-5.8
0.12	72.7	92.4	-19.7
0.08	109.2	125.2	-14.0

RESULTS AND DISCUSSION

EQUIVALENCE-RATIO SWEEP

As discussed in the Experimental section, the engine was configured with a CR = 14 piston, with P_{in} and T_{in} increased to match the TDC conditions of previous studies with CR = 18. Figure 3 shows a plot of the normalized emissions as a function of ϕ . These data were acquired using the conventional emissions-bench analyzers, simultaneously with the detailed speciation measurements. As can be seen, the curves are nearly identical to those in Fig. 1 for CR=18, indicating that the approach of matching TDC conditions results in very similar combustion. The only noticeable difference is that the OHC curve, which is based on the carbon-balance closure (discussed in the Introduction), is flatter. This is mainly due to differences in the CO₂ readings, resulting from a new CO₂ meter, as discussed previously.

Comparison of Total Detailed-Speciation HC and OHC with Emissions-Bench Data – Before presenting the detailed-speciation results, it is useful to compare the total HC and OHC emissions from the detailed-speciation measurements with the emissions-bench data as a cross check on the two data acquisition systems. For this comparison, the detailed speciation data were adjusted to match the expected response of the FID-based analyzer used to obtain the HC emissions-bench data. Accordingly, the total HC from the detailed-speciation measurements includes not only the sum of all the carbon from the HC species, but also the sum of the carbon atoms from the OHC species that are not attached directly to oxygen atoms. Similarly, the total OHC from the detailed-speciation data includes only the carbon atoms that are directly attached to oxygen atoms. (For example, acetone, which contains three carbons and one oxygen, will count as two HC carbon atoms and one OHC carbon atom). This comparison is shown in Fig. 4. Note that the emissions-bench HC and OHC data are the same as those in Fig. 3.

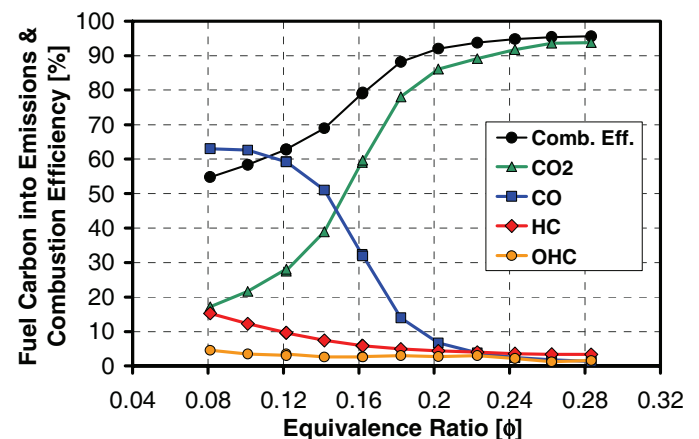


Figure 3. Conventional emissions-bench measurements of global emissions shown as percentage of total fuel carbon. NO_x emissions were near zero and are not reported. CR = 14; P_{in} = 135 kPa; T_{in} was adjusted to obtain CA50 = TDC at each ϕ .