

GC-MS Speciation and Quantification of 1,3 Butadiene and Other C1-C6 Hydrocarbons in SI / HCCI V6 Engine Exhaust

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ABSTRACT

It is known that the levels of hydrocarbon (HC) emissions from Homogeneous Charge Compression Ignition (HCCI) engines are relatively higher than that of Spark-Ignition (SI) engines because of the lower combustion temperature. In order to improve understanding of the mechanisms and products of HCCI combustion in comparison with SI combustion, a quantitative analysis of individual hydrocarbons in the C₁ – C₆ range emitted in the exhaust gases of gasoline direct injection V6 engine operating in SI and HCCI modes with cam profile switching has been carried out using gas chromatography – mass spectrometry (GC-MS) apparatus attached on-line to engine exhaust. In this study, with a GC run time of 20 minutes all aliphatic and olefinic hydrocarbon species in the range C₁ to C₆ are resolved. It is shown that typical 1,3-Butadiene levels in the exhaust of engine operating in SI mode were in range of 9 to 32 µg/g (ppm) for different operation conditions, whereas in contrast, the exhaust from the same engine speed and load in HCCI mode contained almost no 1,3-Butadiene. The common exhaust products of this engine in the two different modes are Methane, Ethylene, Propylene, n-Butane, 1-pentene and n-Hexane at different levels. The total contribution of the lighter species remained practically unaltered when the engine operating parameters were varied, though their individual concentrations did change. The contribution of heavier hydrocarbons (over C₆) attributed to unburned fuel was determined under the same operation condition in the two different combustion modes. The results have shown that the hydrocarbon compounds in range of (C₆ – C₁₂) are responsible for most of hydrocarbon emissions, 50 – 70

% in case of SI mode and 69 – 88 % in case of HCCI mode using the same gasoline fuel and speed/load conditions.

INTRODUCTION

The main focus in the development of IC engines during the years to come will be alternative combustion modes, such as HCCI combustion. Gasoline fuelled (HCCI) engines have the potential to significantly reduce NO_x emissions, and improve fuel consumption compared with Spark-Ignited operation. HCCI is defined as the process in which a largely homogeneous mixture of air and fuel, diluted with excess air as well as combustion products, is compressed under such conditions that auto-ignition occurs near the end of the compression stroke, followed by a combustion process.

Motor vehicles are recognized as a major contribution to the atmospheric burden of hydrocarbons in urban areas, and these have been associated with serious environmental problems such as photochemical smog in addition to harmful effects on human health. It has been concluded that motor vehicles cause approximately 54-58 % of nationwide cancer cause associated with toxic air emissions in the USA [1]. A quantitative assessment for life-time cancer risk made by the US EPA has shown that the unit risk factor for 1,3-butadiene is 30 times larger than that of benzene [2]. Photochemical conversion of 1,3-butadiene to genotoxic products in the presence of nitrogen oxides has been demonstrated [3]. Many reports have appeared on the carcinogenic and mutagenic properties of 1,3-butadiene shown by *in vivo* and *in vitro* studies [4-6]. For these reasons, it should be investigated whether the new generation of HCCI

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engines has potential to reduce emissions of 1,3-butadiene.

The constituents of automobile exhaust comprise compounds in range of C_6 to C_{12} , attributed largely to uncombusted fuel and species formed in the combustion process in range of C_1 to C_5 [7]. In emission research, hydrocarbon speciation is a powerful tool used to understand the combustion process and to observe the effect of varying the gasoline and alternate fuel composition and fuel additives. This lends support to better design of catalytic converters and other emissions control devices, in order to meet the standards required by increasingly strict regulation laws. Studies on hydrocarbon composition in the exhaust gas of SI engines started as early as the late 1960s. Much work has been done using the gas chromatography (GC) technique by researchers in automotive industry and it demonstrates the importance of GC technique in emissions measurement [8-30].

In 1989 a cooperative effort for the Auto/Oil Air Quality Improvement Research Program (AQIRP) produced a well-accepted methodology of HC speciation by gas chromatography by three American automobile companies and 14 petroleum companies. Jensen et al. and Siegl et al. [8, 9] developed a methodology for identification of hydrocarbons and ethers using gas chromatography. Over 140 components between C_1 and C_{12} were analyzed, including alcohols and aldehydes. Kaiser et al. [10-12] showed the influence of six pure paraffin fuels (methane, ethane, propane, n-butane, isopentane and iso-octane), two naphthene fuels (cyclohexane and methylcyclohexane), three aromatic fuels (toluene, xylenes and ethylbenzene), four olefinic fuels (ethylene, 1-butene, 1-hexene and diisobutylene) and two unleaded fuels, on the composition of exhaust hydrocarbons and the fractional contribution of unburned fuel to the total HC emissions in SI engine. These fuels are integral part of commercial gasoline, and being pure, provide results that can be interpreted more easily. Since the early 1990's efforts to improve, simplify, and evaluate the benchmark GC methods have continued [13-22]. In the last decade the American Industry Government Emission Research consortium (AIGER) has been interested in developing more efficient methods for rapidly speciating exhaust hydrocarbons and determining exhaust reactivity. Many works have been published in this area [23-30]. Alas, this rapid GC method includes many complicated instruments and it is highly expensive for conventional laboratories.

Measurements of total exhaust hydrocarbon emissions as a function of engine operating variables in HCCI mode are presented in many publications [31-34].

Christenssen and Johansson examined the THC emission mechanism of HCCI engine operated on iso-octane. The effects of engine operating conditions, combustion phase, and piston top land geometry on THC emissions were examined. It was concluded that most of the THC resulted from unburned fuel released

from the crevices during the expansion stroke [31]. Koopmans and Backlund tested the unburned HC using gasoline fuel. They concluded that measurements of crank angle-resolved unburned HCs showed that a much increased level of unburned HC was produced by a late burning HCCI cycle [32]. Zhao et al. [33] found that the unburned HCs were higher under HCCI mode than SI mode using standard unleaded gasoline of RON 95, while significant reductions were obtained in specific fuel consumption, CO emissions and NO_x emissions. Dec and Sjöberg [34] investigated the CO and THC emissions from an HCCI engine at low load operating on iso-octane. It was found that the emissions of THC and CO increased significantly.

However, there is very limited information available concerning the effects of operating variables and fuel types on the concentrations of individual HC species in the exhaust of HCCI engines.

The effects of the intake temperature, air/fuel ratio, compression ratio, turbo-charging, and EGR rate on exhaust emissions from the HCCI engine operating on n-Heptane were investigated by Li et al. [35] using GC-FID and GC-MSD method. They found that both THC and CO emissions increased significantly when the combustion phasing was retarded, which leads to low combustion efficiency. The results of HC speciation revealed that unburned n-Heptane was the main HC species followed by alkenes, carbonyls and other oxygenates.

Although much progress has been made in the past decade, there are many challenges and technical issues remaining to be resolved before the mass production of HCCI engines. Among the most important issues are: development of suitable fuels for HCCI engines, extension of HCCI engine operational range, control of combustion phasing and emissions control systems to yield a decrease in the mass of emissions from HCCI engines as well as a decrease in their reactivity.

In the present work, a PoraPLOT Q column (porous layer open tubular) was used to measure the low molecular weight hydrocarbons in the range of C_1 to C_6 including the detection of toxic species 1,3-butadiene in engine exhaust gases from a V6 engine operating in SI and HCCI modes, and to measure the amount of unburned fuel among the total exhaust hydrocarbons for several engine running conditions. It is hoped that a more precise quantification of the unburned fuel concentration in the exhaust will aid a better understanding of the whole process of HC production in HCCI mode and will give more background for its control and help in better understanding of the combustion process.

EXPERIMENTAL

The research engine was an advanced prototype of a V6 3.0 litre with dual carburettor switching with a wall

guided direct injection combustion system with a compression ratio of 11.3:1. An electric dynamometer with a motor and a load cell was coupled to the engine and used to load and motor the engine. The engine test rig has been described in detail in previous publications [36, 37]. Air flow to engine is controlled by adjusting the throttle in case of SI mode. In HCCI mode there was no direct method used, the only adjustment was by the inlet and exhaust valve timing. Fuel flow was measured by an AVL Coriolis gravimetric meter, and fuel direct injection pulse width is adjusted by the engine management system to maintain the required value of λ . The fuel used was standard unleaded gasoline of RON 95, H/C = 1.86; composition (saturated = 48.26 %, olefins = 16.2 %, naphthenes 3.66 %, aromatics 30.2 %). An AVL CEB1 analyzer equipped with hot flame ionization detector (FID) and 150 °C heated line was used to measure total hydrocarbons in ppm methane equivalent. Carbon monoxide and carbon dioxide were analyzed by non-dispersive infrared (NDIR) detector and NO_x by chemiluminescence method. Oxygen, λ (air/fuel) ratio, temperature and pressure of the exhaust gases at engine exhaust were also recorded for SI and HCCI modes.

Hydrocarbon speciation was carried out using on-line GC-MS. A Hewlett – Packard Model 5890 Series II GC equipped with direct injector was connected to a TRIO-1 mass spectrometer used as a detector. The gas samples were introduced via unheated line into a six port Valco valve outfitted with a 1 ml sample loop. A 25 metre long x 0.32 mm i.d. capillary column with 10 μ m film thickness PoraPLOT Q was used, which permitted the detection of polar and non-polar compounds simultaneously. After connection of the analytical column in the GC, the column head pressure was set initially to 10 psi. The helium carrier gas flow was pressure controlled with a total flow to the injector of 6ml/min. It was observed that the 15 component standard was generally stable in concentration when the gas was released from the cylinder at this flow rate. Table 1 shows the chromatographic parameters.

Table 1 Gas-chromatographic parameters

Instrument Parameters	HP 5890 series II
Column	Pora POLT Q 25 m; 0.32 mm ID; 10 μ m film
Detector	MS, TRIO-1 Source 200 °C; 10:150 amu
Oven ramp	35 °C initial; 2 minutes hold 8 °C /minute to 130 °C; 2 minutes hold 20 °C / minutes to 220 °C 2 minute final hold (Flush)
Flow rate	6 ml / minute; He

The temperature programme used for the analysis provided for the separation of C₁ to C₆ and for flushing the column.

Standard mixtures of paraffins and olefins from C₁ to C₆ with known concentrations were used to calibrate the chromatograph. Hydrocarbons in the engine exhaust were identified by the use of retention times. The GC retention time scale was calibrated at least daily by analysis of a 15 component gas reference material from British Oxygen Company (BOC). The run time was about 20 minutes and separated species are described in Table 3. Each peak in the chromatogram is related to the amount in weight of organic compound(s) forming that peak.

The VG Mass-Lab software was used to acquire and integrate the basic gas chromatographic data.

Table 2. Retention time of different compounds

Peak number	Compound	Retention Time (min) RT
1	Methane	2.046
2	Carbon dioxide	2.926
3	Ethene	3.856
4	Ethane	4.688
5	Water	6.973
6	Cyclopropane	9.107
7	Propene	9.276
8	Propane	9.776
9	Iso-Butane	14.197
10	1-Butene	14.647
11	1,3-Butadiene	14.787
12	n-Butane	15.167
13	Iso-Pentane	18.437
14	1-Pentane	19.117
15	n-Pentane	19.237
16	n-Hexane	19.738

These are the most important compounds could be detected in the exhaust emissions by this instrument under mentioned conditions and mentioned fuel. Currently studies are also under using BD-1 and BD-5 column to detect heavier hydrocarbons (e.g. Toluene, n-Heptane, Benzene etc.). In the future DNPH method will also be used for the detection of oxygenated compounds. As mentioned in an earlier review from this group [40], the DNPH method is one of best technique for detection of formaldehyde.

EXPERIMENTAL RESULTS AND DISCUSSION

Six speed/load test points were selected for the emissions speciation shown in Table 3, where NMEP is net mean effective pressure. HCCI operates within a limited speeds/loads 'window' compared to conventional SI operation Figure 1. Ways to broaden the HCCI engine operating window have been described in previous publication [38]. The operation conditions, exhaust temperature and emissions data are shown in Tables 3a and 3b.

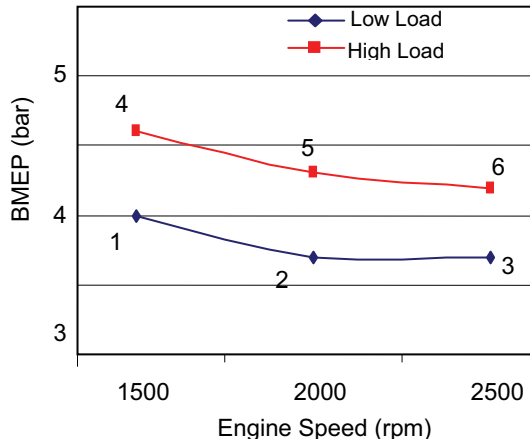


Figure 1. Selected points on speed/load map for this study

Table 3a Operation Conditions and Parameters of V6 Engine in SI and HCCI modes (all for $\lambda=1.0$)

Common conditions			SI mode						HCCI mode					
	Speed rpm	NMEP (bar)	Total HC (FID) ppm CH ₄ equiv	CO %	CO ₂ %	NO _x ppm	O ₂ %	Exh. Temp °C	Total HC (FID)	CO %	CO ₂ %	NO _x ppm	O ₂ %	Exh. Temp °C
(1)	1500	4.0	1010	0.63	13.84	420	1.06	572	1790	0.52	14.01	24	1.19	382
(2)	2000	3.7	930	0.88	13.74	830	1.05	601	1600	0.55	13.92	12	1.19	384
(3)	2500	3.7	910	0.75	13.80	1080	1.02	641	1490	0.68	13.92	14	1.10	398
(4)	1500	4.6	1110	0.69	13.84	630	1.09	591	1400	0.62	14.17	166	0.95	402
(5)	2000	4.3	1030	0.76	13.81	1040	1.07	624	1150	0.63	14.21	104	0.80	404
(6)	2500	4.3	750	0.70	14.36	1140	0.86	662	810	0.47	14.39	163	0.74	432

Table 3b Operation Conditions and Parameters of V6 Engine in SI and HCCI modes (all for $\lambda=1.0$)
Normalized emission values and fuel consumption

Common conditions			SI mode				HCCI mode			
	Speed rpm	NMEP P (bar)	NS HC g/kWh	NS CO g/kWh	NS NO _x g/kWh	Fuel Consumption g/hr	NS HC g/kWh	NS CO g/kWh	NS NO _x g/kWh	Fuel Consumption g/hr
(1)	1500	4.0	7.30	34.8	4.2	3500	12.70	23.6	0.20	2800
(2)	2000	3.7	7.00	41.4	7.8	3900	10.10	25.4	0.09	3100
(3)	2500	3.7	6.10	36.6	9.8	4400	9.10	27.2	0.10	3600
(4)	1500	4.6	7.50	35.2	6.6	4400	8.90	26.7	1.40	3600
(5)	2000	4.3	7.30	36.4	10.0	5100	7.40	27.0	0.80	4200
(6)	2500	4.3	5.40	35.4	11.1	5500	6.00	21.2	1.30	4700

NS = Nett (Indicated) Specific

In case of HCCI mode it can be seen that fuel consumption was reduced by 15-20 % compared with SI mode.