Experimental study on the performance of a three-way catalytic converter in an HCCI engine

Jacek Hunicz^a, Alejandro Medina^b

^a Lublin University of Technology, Lublin, Poland, j.hunicz@pollub.pl ^b Universidad de Salamanca, Salamanca, Spain, amd385@usal.es

Abstract:

The purpose of the current study is to provide comprehensive quantitative data on hydrocarbon species concentrations in exhaust gases from a homogeneous charge compression ignition (HCCI) engine fuelled with gasoline. Additionally, the obtained results yielded assessment of the efficiency of a standard three-way catalytic converter for this kind of engines. Experiments were performed on a single cylinder HCCI engine operated in a negative valve overlap mode, and with direct fuel injection. The engine was run under variable mixture formation strategies, which provided different compositions of cylinder-out exhaust gases. Fourier transform infrared gas analytical system was used for measurements of exhaust gas compositions. The results showed how different injection strategies affect the compositions of unburnt hydrocarbons. Exhaust-fuel reactions resulted in excessive methane production, which reached 9.5% of total unburned hydrocarbons. Measurements of exhaust compositions of hydrocarbons oxidation. Obtained results indicate that besides reduction of regulated toxic compounds, emissions of specific hydrocarbons could be problematic in the light of future applications of HCCI combustion systems.

Keywords:

Homogeneous charge compression ignition, Exhaust emissions, Catalytic converter, Detailed exhaust speciation.

1. Introduction

Homogeneous charge compression ignition (HCCI) is an innovative combustion system, which can be applied in piston engines. Air-fuel mixture is prepared early, thus is well premixed before combustion occurs. The combustion is initiated by temperature during the compression process. Auto-ignition is spontaneous and appears in multiple sites within the combustion chamber. It results in low temperature combustion, as unburnt and burnt mixture zones, typical for other combustion systems, do not appear [1-3]. Volumetric combustion of premixed charge produces extremely low concentrations of nitrogen oxides as well as particulates. In principle, there is no necessity to use advanced exhaust aftertreatment systems, such as selective catalytic reduction or particulate filters [4]. HCCI engines can be equipped with standard three-way catalytic converters, despite lean combustion. Additionally, HCCI engines offer higher thermal efficiency than current spark ignition engines [1].

Conversion of spark ignition engines into HCCI requires introduction of additional energy into the cylinder, to enable auto-ignition of high octane number fuels. This can be achieved by: (i) increasing of compression ratio, (ii) increasing of intake temperature, or (iii) using the exhaust energy [1]. It should be noted, that HCCI combustion at high load regime results in unacceptable pressure rise rates. Thus, gasoline engines have to be operated as spark ignition under high load regimes. The need for switching between two combustion modes limits compression ratio [4]. Thus, utilising of exhaust energy to invoke combustion under low compression ratios appears to be the most attractive from the point of view of practical implementations. Exhaust energy can be introduced into the cylinder via exhaust gas retention, using negative valve overlap (NVO) [4,5]. Engine operated in the NVO mode develops a specific cycle, shown in Fig. 1. Exhaust gas is trapped in the cylinder via early exhaust valve closing (EVC). Afterwards, residuals are re-

compressed during the NVO period. Intake valve opening (IVO) is delayed as well. High amounts of trapped residuals increase mixture enthalpy, and thus enable auto-ignition of gasoline at low compression ratios.



Fig. 1. Typical in-cylinder pressure trace of HCCI process utilising NVO.

Additionally, variable direct fuel injection strategies appear to be effective in combustion controlling due to thermal and chemical effects of exhaust-fuel reactions [6-9]. The introduction of fuel in the early stage of the NVO period (during exhaust compression) enables fuel pyrolysis, which results in the production of auto-ignition promoting species, like ethane, ethylene, acetylene, formaldehyde, and methanol [9-12]. The appearance of these species in the combustible mixture advances the start of combustion by a couple of degrees when compared to mixture formation outside of the cylinder under the same thermal conditions [13,14]. It enables the extension of the engine operating range.

However, low temperature combustion can produce increased emissions of CO and unburnt hydrocarbons (HCs). Despite the fact that approximately 70% of HCs originate from species present in the fuel, exhaust from HCCI combustion can differ from typical exhaust emitted by spark ignition engines [15]. Additionally, variations in hydrocarbons structure in the combustible mixture as a result of NVO fuel injection are reflected in the fractional compositions of the unburned HCs [9]. Thus, special attention should be paid to hydrocarbon species concentrations in exhaust emitted by HCCI engines controlled by direct fuel injection during the NVO period.

The purpose of this study is to provide detailed speciation of hydrocarbon species concentrations in exhaust from HCCI engine where exhaust-fuel reactions were utilised for combustion control. Additionally, the performance of a standard three-way catalytic converter was assessed in reference to particular HC species.

2. Experimental apparatus and method

2.1 – Research engine

A single-cylinder, water cooled research engine was installed on a test bed with a DC dynamometer. The engine was equipped with variable valvetrain which enabled regulation of valves lifts and timings. The regulation of valves lifts was relied on a hydraulic mechanism. The valvetrain was set in order to perform NVO and enable residual effected HCCI combustion. A solenoid swirl-type injector was used for fuel metering directly into the combustion chamber. The main engine parameters are specified in Table 1.

The catalytic converter used in this study was a universal replacement part by Bosal, part No. 099-886. The catalytic converter utilised 45 mm long metal substrate with platinum-rhodium coating. During the research a new converter was used. The converter was located on the exhaust runner approximately 450 mm downstream the exhaust valve. The converter was thermally insulated to reduce cooling by ambient air.

Parameter	Value
No. of cylinders	1
Swept volume	498.8 cm ³
Bore	84 mm
Stroke	90 mm
Geometric compression ratio	11.7
No. of valves	2
Fuel injector	Solenoid swirl type
Fuel rail pressure	10 MPa

Table 1. Engine data

2.2 – Fuel

The fuel used in the study was European Euro Super commercial gasoline with research octane number of 95. The fuel sample was analysed according to ASTM D 5134 standard [16]. The fuel composition is shown in the Table 2. In addition to the species shown in Table 2, fuel contained 4.6% of ethyl tert-butyl ether and 5% of ethanol. The overall carbon to hydrogen ratio on the mass basis was 6.43 and atomic hydrogen to carbon ratio was 1.85. The average formula of the fuel would be $C_{6.33}H_{11.73}O_{0.14}$ and molecular weight was approximately 90 g/mole. Theoretical stoichiometric air-fuel ratio (AFR) was 14.22 on the mass basis.

Number of atoms C, %	Alkanes, %	Cycloalkanes, %	Alkenes, %	Aromatics, %
4	0.35	-	0.32	-
5	11.53	0.52	5.3	-
6	12.1	2.81	2.04	0.89
7	4.71	1.35	-	8
8	3.7	2.35	-	11.67
9	0.32	0.18	-	9.29
10	0.12	-	-	0.43
Other	4.79	0.53	-	6.78
Total	37.62	7.74	7.66	37.06

Table 2. Fuel composition

2.3 – Measurement equipment

The engine test bench was equipped with all the necessary measurement and control instrumentation. The engine dynamometer and the engine control system were fully automated. However, during measurements all control values, besides rotational speed and temperature control, were fixed constant. Detailed exhaust gas compositions were analysed with the use of an AVL Sesam FTIR multi-compound analytical system. The device used a scanning Michelson interferometer. Spectra of infrared light absorbed by a gas sample were recorded in a wavelength range of 700 to 4000 cm⁻¹ with an optical resolution of 0.5 cm⁻¹. 20 different exhaust gas components were detected simultaneously. In the range of unburned hydrocarbons and nitrogen oxides, the concentrations of individual chemical compounds were analysed. Exhaust gas was delivered to the measurement chamber of the interferometer with the use of a heated lines system

and a 4-way heated sample switch unit with a ceramic heated filtering element. The heated gas sampling system was operated at a constant temperature of 185 °C. The recorded spectra were compared with spectra obtained from ambient air, dried and filtered from carbon dioxide, flowing through the filter and the sampling lines. This excluded the influence of deposits in the filter and the sampling lines. The measurement errors of the analytical system in case of hydrocarbons varied from 0.1% to 0.49%, depending on species. The given accuracies are average values over concentration span from 0 to 1000 ppm. Measurement error of CO was 0.31% from 0 to 4000 ppm, whereas for NO, an average error was 0.36% in the range from 0 to 10000 ppm.

Air-fuel ratio of the mixture was measured by a Bosch LSU 4.2 wide band oxygen sensor located in the exhaust runner and an Etas LA4 lambda meter. Exhaust temperature was measured with the use of a thermocouple located in the exhaust runner approximately 50 mm downstream the exhaust valve. A schematic diagram of the experimental test stand is shown in Fig. 2.



Fig. 2. Schematic diagram of the experimental test stand.

Thermodynamic analysis of in-cylinder processes is not a subject matter of this study; however, some important parameters were computed on the basis of pressure traces. Pressure was measured with the use of a miniature pressure transducer mounted directly in the engine head. A data recording system for pressure and other crank angle based parameters was triggered by optical crankshaft encoder with angular resolution of 0.1 crank angle degrees (CAD). Engine load was expressed using indicated mean effective pressure (IMEP), computed as the ratio of indicated work and swept volume of the cylinder. Additionally, in-cylinder pressure was used for the calculation of the amount of trapped residuals. The mass of exhaust inside the cylinder at EVC event was obtained from the gas equation of state on the basis of in-cylinder pressure, temperature in the exhaust port, and in-cylinder volume. Internal exhaust gas re-circulation rate was computed as the ratio of the mass of trapped residuals and the entire in-cylinder mass during the main event, including fuel.

2.4 – Experimental conditions and procedure

The experiments were conducted at an engine speed of 1500 rev/min and wide open throttle. The engine was naturally aspirated and the intake air was heated up by a water jacket around the intake pipe up to a temperature of approximately 40 °C. The temperature of the cooling liquid at the engine outlet was maintained constant at 90 °C \pm 1.

Four engine operating conditions were investigated in this study. Two different valvetrain settings were applied, as shown in Table 3. To simplify imaging crank angle based figures, all timings are given in terms of degrees after NVO top dead centre (TDC), as in Fig. 1. The applied valve timings provided different amounts of trapped residuals, and thus, different internal exhaust gas recirculation (EGR) rates. At each engine load two mixture formation strategies were utilised: (i)

early NVO injection, and (ii) late NVO injection. In both cases all fuel was injected in a single dose. Early NVO injection was applied at a start of injection (SOI) timing of -40 °CA. Earlier studies showed that to a high extent exhaust-fuel reactions happen at this injection timing [8]. As a result, high concentrations of pyrolysis products were observed in combustible mixture. Additionally, the modification of fuel affected the fractional composition of unburnt hydrocarbons in exhaust gases [9]. Late NVO injection was applied at SOI timing of 20 °CA. This injection timing did not provide exhaust-fuel chemical reactions, whereas thermal effect of fuel vaporization on NVO mixture was similar. For all the investigated cases a slightly lean mixture was applied, to enable oxidation of hydrocarbons in the catalytic converter. AFR was approximately 16.5, where stoichiometric AFR was 14.22.

Parameter	Case 1	Case 2	Case 3	Case 4
IVO (°CA)	83	83	89	89
IVC (°CA)	213	213	219	219
EVO (°CA)	527	527	508	627
EVC (°CA)	646	646	508	627
NVO (°CA)	157	157	182	182
SOI (°CA)	20	-40	20	-40
IMEP (MPa)	0.353	0.329	0.266	0.236
AFR (-)	16.38	16.57	16.4	16.37
EGR, %	31.7	37.2	49.9	53.4
Exhaust temperature (K)	861	815	761	736

Table 3. Engine parameters

Table 3 shows the values of the control variables, mixture compositions, and engine loads under research conditions. It should be noted that the amount of trapped residuals controls fresh air aspiration [5]. Thus, larger NVO angles, which provided larger amounts of residuals, resulted in a reduction in fresh air aspiration. As a result, valve timings affected engine load expressed by IMEP, as shown in Table 3. It can be also noted how injection timing influences gas exchange and engine load. For cases with early NVO injection, higher EGR rates and lower IMEP values were observed. This observation can be attributed to the thermal effects of exhaust-fuel reactions.

3. Results and discussion

3.1 – Cylinder-out emissions of regulated toxic compounds

Current emission standards introduce limitations of emissions so-called regulated toxic compounds. Among gaseous compounds, limitations consider production of carbon monoxide and cumulative groups of other toxic compounds, i.e. nitrogen oxides and unburned hydrocarbons.

The total content of unburned HCs is not provided by a FTIR analyser, however, it was computed as a weighted sum of all detected hydrocarbons, and expressed as C_1 on the mole basis. Fig. 3 shows that total HC (THC) content is affected both, by NVO duration as well as injection timing. In general, early injection reduced concentration by 20 - 30%. Clearly, at lower load HC concentrations increased due to the decrease of combustion temperature. It should be noted that obtained concentrations of HCs were relatively high. In terms of emission index, unburned HCs constituted from 1.9% to 3.6% of fuel injected. However, it should be noted that the combustion chamber of the research engine was not optimised to reduce hydrocarbons emissions. The piston shape provided a large squish area, which was a source of additional HC emissions due to crevice quenching effects. The detailed speciation of hydrocarbons emitted with exhaust gases is discussed in the next subsection. In general, HCCI engines emit high CO concentrations in exhaust gases. The reason for this disadvantage is low in-cylinder temperature, which brings the end of CO oxidation at the latter stage of the combustion process. Nevertheless, the emissions of CO recorded in the current study were very small for all the conditions that were investigated, despite the mixture was always highly diluted. It should be noted that early injection slightly increases CO concentrations. This is plausible, as CO is produced as a result of NVO exhaust-fuel reactions. Thus, it can be a consequence of quenching effects, as in the case of HCs.



Fig. 3. Concentrations of regulated toxic compounds upstream the catalytic converter.

Although FTIR detects different NO_X species, they will not be discussed in detail. It is enough to mention that they are constituted mainly by NO under all investigated conditions. Fig. 3 shows that relatively high NO_X concentrations appeared at higher load. Such concentrations are typical of exhaust from diesel engines under similar conditions. It should be noted, however, that diesel engine was operated at near-stoichiometric conditions, thus emissions were few times lower than emissions from diesel engines. Comparison of NO_X concentrations for two investigated loads shows how their production is sensitive to mixture dilution by exhaust gas. An increase in EGR rates by larger NVO duration reduced NO_X concentrations by 93%-94%. Such a dramatic drop in NO_X concentrations were small. The reason for this behaviour was the advance of combustion for early injection, which also affected the peak temperature. As a result, there was some kind of balance between the factors which increase or decrease NO_X production.

3.2 – Detailed speciation of hydrocarbons in cylinder-out exhaust

Exhaust-fuel reactions which take place during the NVO break long-chained hydrocarbons and produce methane, light unsaturated hydrocarbons, and aldehydes [9-12]. Thus, it is plausible that changes in the fuel composition can modify exhaust hydrocarbons structure. This issue is very important because some products of exhaust-fuel NVO reactions have very harmful effects. Fig. 4 shows mole fractions of hydrocarbons and oxygenated hydrocarbons displayed by FTIR analyser. It can be noted that sum of concentrations shown in Fig. 4 is smaller than numbers shown in Fig. 3, as in the latter concentrations are expressed as C_1 .

Methane is one of the products of NVO fuel reactions. Direct measurements of the NVO gas compositions have shown high impact of NVO injection timing on CH₄ production [9]. Under comparable engine operating conditions, concentrations varied from approximately 150 ppm at late

injection to 2000 ppm for early injection [17]. At early NVO injection and under certain conditions, even 7% of fuel can be converted into CH₄ [9]. Fig. 4 shows that changes in the fuel structure as a result of exhaust-fuel reactions are reflected in the hydrocarbons composition of the exhaust gases. Early injection increases CH₄ concentration in the exhaust gas by a factor 4-5 when compared to late injection cases. It should be also noted that higher EGR rates enhance CH₄ production. For Case 4 indicated specific emission of methane reached 0.7 g/(kW·h) and constituted 9.5% of total unburned hydrocarbons on the mass basis.



Fig. 4. Concentrations of hydrocarbons and oxygenated hydrocarbons upstream the catalytic converter.

Likewise CH₄, productions of acetylene and ethylene were enhanced by early injection and higher EGR rates. Acetylene is one of the most effective products in terms of auto-ignition properties improvement, which is produced by exhaust-fuel reactions during the NVO period [12,13]. Concentrations of ethane decreased for early NVO injection. Trend in propene concentrations were similar to methane and light unsaturated hydrocarbons, however relative changes were much less affected by injection strategy.

Among different hydrocarbons emitted by combustion processes, 1,3-butadiene is of the highest importance due to its carcinogenic potential. C_4H_6 is considered one of the most harmful among all toxic compounds emitted by motor vehicles [18,19]. The trend in concentrations of 1,3-butadiene is similar to that one of methane and other light unsaturated hydrocarbons. For Case 4 concentration of C_4H_6 was as high as 21 ppm, which constituted 2.9% of THC on the mass basis.

Emissions of heavier hydrocarbons detected by the FTIR analyser, i.e. n-pentane, isopentane and toluene, which represented all aromatics in FTIR measurements, under investigated conditions changed contrarily to lighter hydrocarbons, as shown in Fig. 4. Application of early NVO fuel injection reduced concentration of pentanes collectively by 45%-67%, whereas the content of aromatics was only reduced in a small extent of about 11%-23%. The trade-off between light and heavy hydrocarbons for both injection strategies that were applied resulted from variations in their concentrations in the combustible mixture, as their emissions come only from the respective fuel components [20,21].

Emissions of oxygenated hydrocarbons are also worth notice. Among them, formaldehyde is the second harmful, after C_4H_6 , gas emitted by motor vehicles [19]. It should be noted that high production of this compound was identified as a result of exhaust-fuel reactions during the NVO period [17]. However, HCHO content in the exhaust gas has been found neither affected by EGR rate nor by the injection timing. Concentrations of acetaldehyde were slightly higher for late

injection than for early injection, whereas in the combustible mixture its concentration was twice higher for the latter.

3.3 – Performance of the catalytic converter

The conversion efficiency of the catalytic converter was expressed using the following formula:

$$\frac{\tilde{x}_{upstream} - \tilde{x}_{downstream}}{\tilde{x}_{upstream}} \times 100\%, \qquad (1)$$

where \tilde{x} is the mole fraction of a specific compound or group of compounds upstream or downstream the catalytic converter.

Figure 5 shows the conversion efficiency of the considered catalytic converter (details are given in Sec. 2.1) under research conditions. It should be noted that for all investigated cases, conversion of hydrocarbons was low, as a result of low exhaust temperatures. Table 3 shows that temperatures varied from 761 K to 861 K. Also notice that the conversion efficiency was not affected by exhaust temperature to a high extent. Exhaust temperatures for the cases with higher EGR rates were between 80 K and 100 K lower than for the cases with lower EGR, as shown in Table 3. However, this temperature difference resulted in only a few percent reduction in efficiency. For the cases with early NVO injection, where extensive species production during the NVO period was observed, hydrocarbons conversion was more efficient, despite lower exhaust temperature. In principle, low performance of hydrocarbons oxidation concerns all engines which produce exhaust gases at low temperatures, e.g. diesel engines under low loads [22]. In contrast, exhaust of stoichiometric spark ignition engines have much higher temperatures, thus catalytic efficiency usually exceeds 90%.



Fig. 5. Catalytic efficiency of regulated toxic compounds.

In case of CO, conversion efficiency exceeded 90%, despite low temperature. The difference between conversion of hydrocarbons and CO results from different light-off temperatures¹ of these compounds. For CO, the light-off temperature of a typical converter is as low as 420 K, whereas oxidation of hydrocarbons starts between 480 K and 800 K [23-25].

Under the basis of a lean mixture regime it was not expected to achieve any reduction of NO_X . Nevertheless, between 16% and 27% of NO_X was removed by the catalytic converter.

Because different hydrocarbons oxidise at different temperatures, it is important to analyse catalytic efficiency for different hydrocarbons species. Additionally, it was shown in Sec. 3.2 that the composition of unburned HCs from HCCI combustion with direct fuel injection during exhaust

¹ Light-off temperature is a temperature of catalytic converter at which 50% conversion efficiency is reached.

compression modified the fractional composition of HCs to a high extent. Thus, under certain conditions, emissions of specific hydrocarbons can be high along with low catalytic efficiency.



Fig. 6. Catalytic efficiency for hydrocarbons and oxygenated hydrocarbons.



Fig. 7. Catalytic efficiency for CH_4 versus concentration of C_2H_2 upstream the catalytic converter.

Among different hydrocarbons, methane poses a challenge as it has a much larger negative greenhouse effect than CO₂. Unfortunately, light-off temperature of CH₄ is high, at around 800 K [26], while under investigated conditions temperature at engine outlet varied between 736 K and 861 K. Fig. 6 shows that CH₄ conversion degrees were very low. For Case 4 even production of CH₄ was noted. It was demonstrated in [23] that conversion of some species can be inhibited by other species. Among species shown by the FTIR analyser, acetylene exhibits strongly inhibiting effect. As exhaust temperatures observed during experiments were around light-off temperature of CH₄, it was expected that catalytic efficiency can be affected by both temperature and C₂H₂ content. Correlation between methane conversion and C₂H₂ concentration is presented in Fig. 7. These data are divided into two groups according to exhaust temperature; below and above methane light-off temperature. It can be noted from the graph that apart from temperature, conversion of CH₄ is

strongly affected by C_2H_2 concentration. At the same time, conversion of acetylene itself is very high, increasing with its concentration.

Other light HCs exhibit high conversion efficiency. However, oxidation of pentanes is lower than other hydrocarbons. Iso-pentane exhibits very low conversion rates, additionally with a trend similar to the one observed for methane, which can be also attributed to the inhibiting effect of acetylene.

4. Conclusions

The present study explored the emissions of a gasoline-fuelled HCCI engine. To induce HCCI combustion, the NVO technique was applied. The engine was run at different internal exhaust gas re-circulation rates and under slightly lean mixture conditions. Fuel was injected during the NVO period at two timings, where early NVO injection resulted in extensive exhaust-fuel reactions, which produce methane, light unsaturated hydrocarbons and aldehydes. A Fourier transform infrared gas analyser was used for detailed speciation of hydrocarbons upstream and downstream of the three-way catalytic converter. It was found that direct fuel injection strategies and composition of NVO mixture have a great impact on the fractional structure of unburnt hydrocarbons. Additionally, a standard three-way catalytic converter exhibits low hydrocarbon conversion performance under low exhaust temperatures, typical of HCCI engines. The detailed results of the studied conditions can be summarized as follows:

- Early NVO injection results in a substantial increase in the emission of methane when compared to late injection. Additionally, an increase in the amount of trapped residuals enhances the production of CH₄. For early NVO injection and higher internal EGR rate, methane constituted 9.5% of the total unburnt hydrocarbons on the mass basis.
- High emissions of methane in raw exhaust can be problematic from the point of view of the performance of three-way catalytic converters. CH₄ has high light-off temperature, thus observed catalytic efficiency was low at low exhaust temperatures, typical of HCCI engines. Additionally, acetylene, which exhibits inhibiting effects, reduced converter efficiency to a high extent.
- Cylinder-out emissions of light unsaturated hydrocarbons (acetylene, ethylene, propene and 1,3butadiene) are, likewise emission of methane, increased by both early injection and increase in the amount of trapped residuals. Concentration of environmentally harmful 1,3-butadiene exceeded 20 ppm, however, approximately 90% of this compound was removed by the catalytic converter under all investigated conditions.
- Emissions of aldehydes were not affected neither by the injection strategy nor by the amount of trapped residuals, besides the fact that their concentrations in the combustible mixture were determined by the injection timing.
- Application of early NVO injection reduced emissions of pentanes by approximately 45%-67% and aromatics by 11%-23%, when compared to late fuel injection. These exhaust species are originated directly from fuel compounds, thus the reduction in their concentrations resulted from the modification of the fuel during NVO. However, in the case of pentanes, low performance of catalytic converter was noted.

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