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Original Research

Detailed Speciation of Emissions from Low-Temperature Combustion in a Gasoline HCCI Engine

Jacek Hunicz[1], **Paweł Krzaczek**[2]*

[1]Institute of Transport, Combustion Engines and Ecology, Lublin University of Technology,
Nadbystrzycka 36, 20-618 Lublin, Poland
[2]Department of Power Engineering and Transportation, Faculty of Production Engineering,
University of Life Sciences in Lublin,
Głęboka 28, 20-612 Lublin, Poland

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Abstract

This study relates to a detailed speciation analysis of hydrocarbon emissions from a homogeneous charge compression ignition (HCCI) engine utilizing negative valve overlap (NVO). A split fuel injection technique is employed, where the first injection is applied during exhaust re-compression and the second injection is applied at the beginning of the main compression. Quantities of fuel injected at the two timings are varied, from the whole fuel injection during NVO to the whole fuel injection during the main compression event. These split-fuel ratio sweeps are repeated both for a stoichiometric mixture and for a slightly lean mixture to determine the effect of an excess air ratio on emissions. It has been found that the employed injection strategy has a great impact on hydrocarbon composition in an exhaust gas as a result of the NVO exhaust-fuel reactions. Fuel injection in an early stage of NVO results in an excessive emission of 1,3-butadiene. Additionally, high emissions of methane are observed, but solely in the lean mixture regime.

Keywords: HCCI, gasoline, direct injection, negative valve overlap, hydrocarbon speciation

Introduction

Increasing environmental concern regarding the use of automotive vehicles and non-road machinery powered by combustion engines has drawn worldwide attention to the problem of reducing harmful effects of exhaust emissions [1-3]. The main toxic compounds regulated by the emission standards for combustion engines fuelled by hydrocarbon fuels are carbon monoxide, nitrogen oxides, unburnt hydrocarbons, and particulate matter. Among these general groups of compounds, one should note a large variety of hydrocarbons and oxygenated hydrocarbons in exhaust gases [4]. Different hydrocarbons exhibit different effects on human health. Despite a great effort to understand the various negative effects, there is still a lack of comprehensive knowledge in this field [5]. As for the group of hydrocarbon species, 1,3-butadiene and formaldehyde are considered to exert the most harmful effect. However, other aldehydes, benzene, and toluene are also considered to be substances that increase the risk of heart disease, lung disease, and cancer [5–7]. It should also be emphasized that particulate matter can be of a different chemical composition and size, which adds to its harmful effects [8, 9].

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*e-mail: pawel.krzaczek@up.lublin.pl

Both the current and forthcoming legislative requirements have prompted a search for solutions to improve the existing engines [10] and to develop more efficient exhaust after-treatment systems [11]. In parallel to this, alternative fuels including biofuels are widely utilized to reduce CO_2 emissions [1, 4, 12, 13].

In addition to the above, innovative engines other than spark ignition or diesel engines are being developed at the same time. Among numerous concepts of engine and combustion systems, low temperature combustion (LTC) seems to be the most attractive due to extremely low emissions of nitrogen oxides and particulates [14]. LTC combustion can be successfully realized in homogeneous charge compression ignition (HCCI) engines, where the mixture is prepared well before combustion, so it is well premixed prior to ignition. Ignition is compression-affected and it appears spontaneously at multiple sites of the combustion chamber. Such a course of the combustion process is characterized by a lack of flame propagation and uniform temperature across the cylinder. Also, as combustion is kinetically controlled, it is very quick, resulting in a realization close to the ideal Otto cycle. Due to these features, HCCI combustion exhibits an uncompromising improvement in terms of thermal efficiency and reduction of cylinder-out emissions [15-17]. HCCI engines can accomplish even future emission standards using solely three-way catalytic converters [18, 19]. It should also be noted that HCCI combustion systems tolerate nearly all oil-based and alternative fuels exhibiting various auto-ignition properties [12, 17, 20].

A solution which seems the most feasible regarding HCCI engines is internal exhaust gas re-circulation (EGR) utilizing negative valve overlap (NVO) [18]. This technique allows auto-ignition of high-octane number fuels (gasoline-like) at compression ratios that are typical of spark ignition engines [19]. HCCI engines operated in the NVO mode realize a specific cycle, as shown in Fig. 1. Exhaust gas is trapped in the cylinder via early exhaust valve closing (EVC). Afterward, residuals are re-compressed during the NVO period. Intake valve opening (IVO) is delayed as well. High amounts of trapped residuals increase mixture enthalpy, thereby enabling auto ignition of gasoline at low compression ratios.

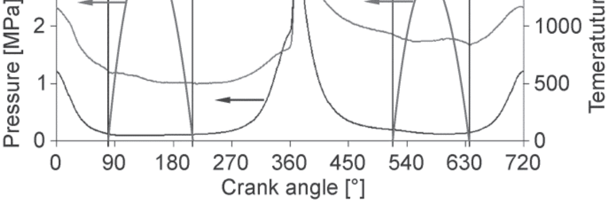


Fig. 1. In-cylinder pressure, temperature, and valve lifts of HCCI engine operated in NVO mode.

Table 1. Research engine specifications.

Displaced volume	498.5 cm^3
Stroke	84 mm
Bore	90 mm
Compression Ratio	11.7
Number of Valves	2
Intake Valve Lift	3.6 mm
Intake Valve Open (IVO)	82 CAD
Intake Valve Close (IVC)	212 CAD
Exhaust Valve Lift	2.9 mm
Exhaust valve Open (EVO)	515 CAD
Exhaust Valve Close (EVC)	634 CAD
Negative Valve Overlap	168 CAD

Ignition and combustion processes in HCCI engines are mainly governed by chemical kinetics of hydrocarbon oxidation. Auto-ignition timing is primarily controlled by compression temperature histories. It is also affected by mixture composition and its ignitability [21]. However, it should be noted that the aforementioned parameters can be neither separately nor directly controlled in practical engines. Hence, the control of combustion timing under variable operating conditions is the most crucial problem in the development of HCCI engines [22].

Variable direct fuel injection strategies appear to be effective in combustion control due to thermal and chemical effects of exhaust-fuel reactions [23, 24]. The introduction of fuel in an early stage of the NVO period (during exhaust compression) enables fuel reforming, which results in the production of auto-ignition-promoting species like ethane, ethylene, acetylene, formaldehyde, and methanol [25-28]. The occurrence of these species in the combustible mixture advances the start of combustion by several degrees when compared to the mixture preparation outside of the cylinder under the same thermal conditions [29, 30]. However, thermal NVO processes are widely recognised as dominant in combustion control [23, 25]. Nevertheless, the utilization of direct fuel injection for combustion control and extension of engine operating range into a low load regime causes chemical modifications of fuel. Clearly, variations in hydrocarbon structure in the combustible mixture are reflected in the fractional compositions of the unburned hydrocarbons [25]. Thus special attention should be paid to species concentrations in exhausts emitted by HCCI engines controlled by direct fuel injection during the NVO period.

The purpose of this study is to provide comprehensive quantitative data on hydrocarbon species concentrations in exhaust gases from HCCI engine fuelled with gasoline. Additionally, the results are discussed in the aspect of potential harmful effects of hydrocarbon species.

Experimental Setup and Procedure

Experimental Test Stand

The experiments in this study were conducted using a dedicated single cylinder research engine. The engine was built in-house using a special hydraulic engine head design enabling the adjustment of valve timings and valve lifts. This fully variable valvetrain was set to achieve NVO, and thus engine operation in the HCCI mode. The engine specifications along with the valvetrain settings applied in the experiments are listed in Table 1. Fuel was directly injected into the combustion chamber using a solenoid swirl-type injector. A more detailed description of the combustion system and the valvetrain utilized in the experimental engine can be found in [31]. The engine was mounted on a test bench equipped with a direct current dynamometer controlled by an automation system. Fig. 2a shows a photograph of the experimental engine and Fig. 2b shows a schematic design of the experimental setup.

The engine test bench was equipped with all necessary measurement and control instruments. The composition of exhaust gas was measured using an AVL Sesam FTIR multi-compound analytical system. Additionally, the oxygen content in the exhaust gas and excess air ratio (l) were measured by a wide-band oxygen probe installed in the exhaust runner and interconnected with an ETAS LA4 lambda meter. In-cylinder pressure was measured with a constant angular resolution of 0.1 crank angle degree (CAD) using a miniature pressure transducer and a charge amplifier.

Fuel Specifications

The fuel used in the study was European Euro Super commercial gasoline with a research octane number of 95. The fuel sample was analysed according to the ASTM D 5134 standard [32]. The fuel composition is given in Table 2. In addition to the species shown in Table 2, the fuel contained 4.6% ethyl tert-butyl ether and 5% ethanol. The overall carbon-to-hydrogen ratio on the mass basis was 6.43 and the atomic hydrogen-to-carbon ratio was 1.85. The average formula of the fuel was $C_{6.33}H_{11.73}O_{0.14}$ and molecular weight was 90 g/mole.

Table 2. Fuel composition in % on the mass basis CAD-crank angle degree.

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

Experimental Conditions and Procedure

The experiments were conducted at an engine speed of 1,500 rev/min at wide open throttle. The engine was naturally aspirated and the intake air was heated by a water jacket around the intake pipe to a temperature of approx. 40ºC. The cooling liquid temperature at the engine outlet was maintained at a constant 90ºC ±1.

The fuel was introduced into the cylinder at two selected start of injection (SOI) timings. In order to enable fuel reforming, the NVO injection was applied at SOI = 40 CAD before top dead centre. The second injection was applied with an SOI timing of 240 CAD at the beginning of the compression process. The fuel pressure before the in-

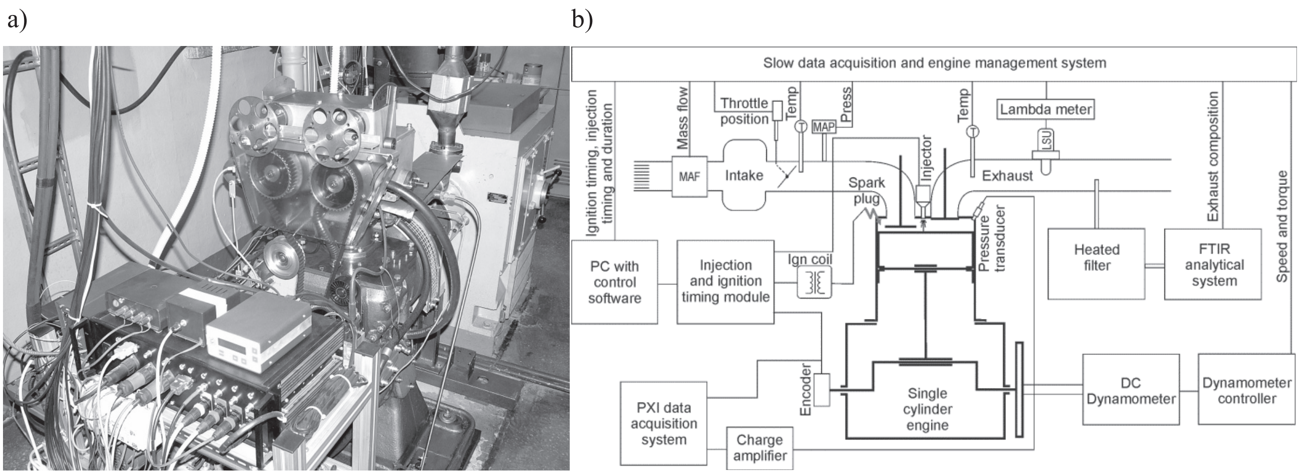


Fig. 2. Experimental test stand: a) photo, b) schematic design.

jector was set to 10 MPa. At this pressure, the fuel delivery rate was 8.89 g/s, which corresponded to approximately 1 mg/CAD at an engine speed of 1,500 rev/min.

The employed fuel injection strategies were varied, from whole fuel injection during NVO to whole fuel injection during compression. The split ratios presented in the graphs are shown as the ratio of mass of NVO fuel injection to entire fuel injected. The experiments were performed for two mixture strengths: for a stoichiometric mixture and for excess air ratio $\lambda = 1.2$, controlled via the amount of fuel injected.

At each measurement point, the engine was running under steady conditions; engine temperature and speed control procedures were the only parameters left active. The reported values of species concentrations and excess air are mean values computed from 60-second measurement periods. The parameters derived from the in-cylinder pressure were calculated separately from 100 consecutive cycles and then averaged.

Thermodynamic analysis of the engine cycle is not a subject of this study. However, some calculations based on the in-cylinder pressure traces were necessary for estimating main engine parameters. The mass of trapped residuals was calculated using the ideal gas equation of state based on the volume (V_{EVC}), pressure (p_{EVC}) at the EVC event, and exhaust temperature (T_{exh}) according to Eq. 1.

$$m_{exh} = \frac{p_{\mathrm{EVC}} V_{\mathrm{EVC}}}{R T_{exh}} \quad (1)$$

… where R is a specific gas constant of the exhaust gas computed according to its composition.

The exhaust temperature was provided by a thermocouple located in the exhaust port close to the valve. This approach is commonly used for estimating exhaust mass trapped in the cylinder and the obtained data correspond with those from the direct measurements [33]. Additionally, we introduced the corrections proposed by Fitzgerald et al. [34] in order to compensate for the effect of exhaust expansion which occurs on flowing through a valve. EGR rates were calculated on the mass basis as a ratio of trapped residuals and the entire in-cylinder load during the main event.

The indicated mean effective pressure (IMEP) was utilized to express the engine ability to do work. This measure is independent of cylinder size and it is calculated from the in-cylinder pressure (p) and volume (V) using the following formula:

$$\mathrm{IMEP} = \frac{1}{V_S} \oint p\, dV \quad (2)$$

… where V_S is the swept volume of the cylinder.

Results and Discussion

NVO Mixture Composition

In order to provide conditions for fuel modifications that affect species concentrations in exhaust gases, it is necessary to know NVO mixture composition. The effects of mixture strength and thermal NVO fuel-exhaust processes on gas exchange and mixture composition are quite complex; however, they were already studied in numerous works (e.g., in [19, 27]). A rule of thumb is that an increase in the main event λ increases the amount of trapped residuals due to a lower exhaust temperature and the resulting higher density. Direct fuel injection during the NVO period introduces further complexities into the gas exchange. At lean mixtures, the heat release during NVO reduces the amount of fresh air due to an increase in IVO pressure and temperature.

It can be noted in Fig. 3 that for $\lambda = 1.2$, the EGR rate is almost constant for all the applied fuel split ratios. This suggests that the heat consumption for fuel vaporization and the possible endothermic reforming are compensated for by heat release, which means that the same thermodynamic conditions are maintained at the end of NVO. At stoichiometric mixture, a reduction in fuel mass injected during NVO led to an increase in the EGR rate. Here, the heat release was negligible due to a deficiency of oxygen. At the same time, the reduced amount of NVO fuel resulted in lower heat consumption, higher IVO temperature, and a lower amount of aspirated air. For the stoichiometric mixture case, the mass of fuel injected in order to maintain the desired λ value was gradually reduced from 12.9 mg for the whole fuel injected during NVO to 11 mg for the whole fuel injected during compression. This was due to the cooling effect of fuel injection, which improves

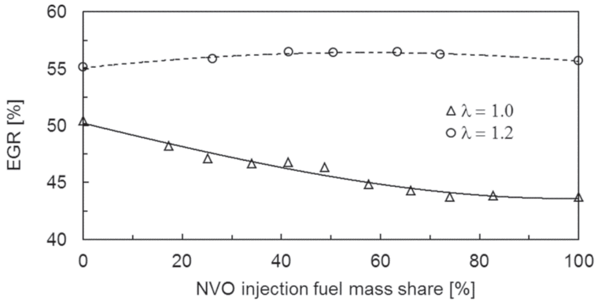


Fig. 3. EGR rate with respect to NVO injection fuel mass share.

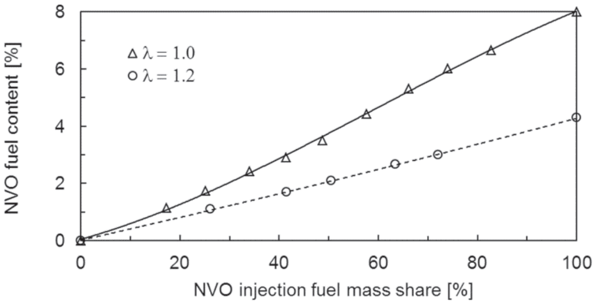


Fig. 4. Fuel content after NVO injection with respect to NVO injection fuel mass share.

volumetric efficiency. At λ = 1.2 the mass of fuel was in all cases nearly constant, ranging between 8.4 and 8.7 mg per engine cycle. Fig. 4 shows NVO fuel-exhaust proportions by mass. Due to the effect of λ on EGR, the range of fuel-exhaust ratio is higher than that resulting solely from the main event excess air.

Engine Load and Combustion Course

Engine loads achieved in the experiments were low due to high rates of internal EGR, not to mention the wide-open throttle. For a stoichiometric mixture, IMEP varied from 0.34 MPa for early injection to 0.27 MPa for late injection, due to the variability in mass of fuel (shown in the previous subsection). In contrast, for a lean mixture, apart from a nearly constant mass of fuel, the engine load increased from 0.2 MPa to 0.23 MPa when NVO fuel was reduced. This effect can be ascribed to heat release during the NVO period. The more fuel was injected early, the more heat was released, thereby reducing the indicated work of the main event. As a result, the overall thermal efficiency of the engine was reduced.

The effects of excess air and split fuel injection ratio on combustion evolution are illustrated in Fig. 5 by in-cylinder pressure traces during the main event. Under stoichiometric conditions, the combustion timing revealed a non-monotonous response to variable fuel split ratios, as shown in Fig. 5a. With the whole fuel injected at an early stage of NVO, early auto-ignition was observed. However, in split fuel injection when high amounts of fuel were being delivered during NVO, we observed a delay of auto-ignition by approx. 4 CAD. A further reduction in the NVO fuel advanced auto-ignition. At lean mixture, the more fuel injected early, the earlier auto-ignition was observed (Fig. 5b) due to the effect of heat release during the NVO period.

Consideration of Regulated Toxic Compounds

Under lean mixture conditions, the emissions of CO were practically independent of the employed fuel injection strategy, as shown in Fig. 6a. The CO content was kept between 3,000 and 2,000 ppm, which was equivalent to 33 to 48 grams per kilogram of fuel. At stoichiometric mixture, the CO content decreased from 7,950 ppm for all fuel injected during the main event to 1,650 ppm for all fuel injected during NVO. Even though CO is the main reforming product, the observed trends resulted primarily from the main event phenomena. Late fuel injection provided mixture stratification, which led to incomplete combustion under stoichiometric conditions.

The content of total unburned hydrocarbons (THC) was not provided by the FTIR analyzer; however, it was computed as a weighted sum of all detected hydrocarbons and expressed as C_1. Fig. 6b shows that

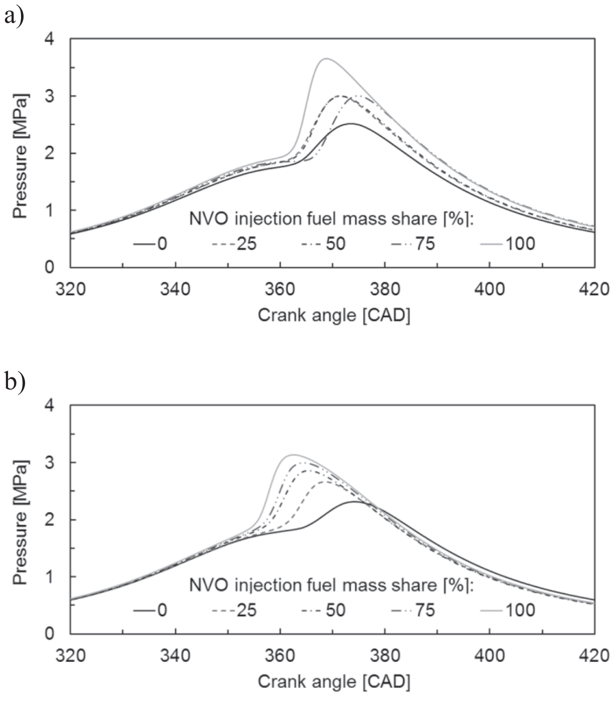


Fig. 5. In-cylinder pressure during the main event for variable NVO fuel: a) λ = 1.0, b) λ = 1.2.

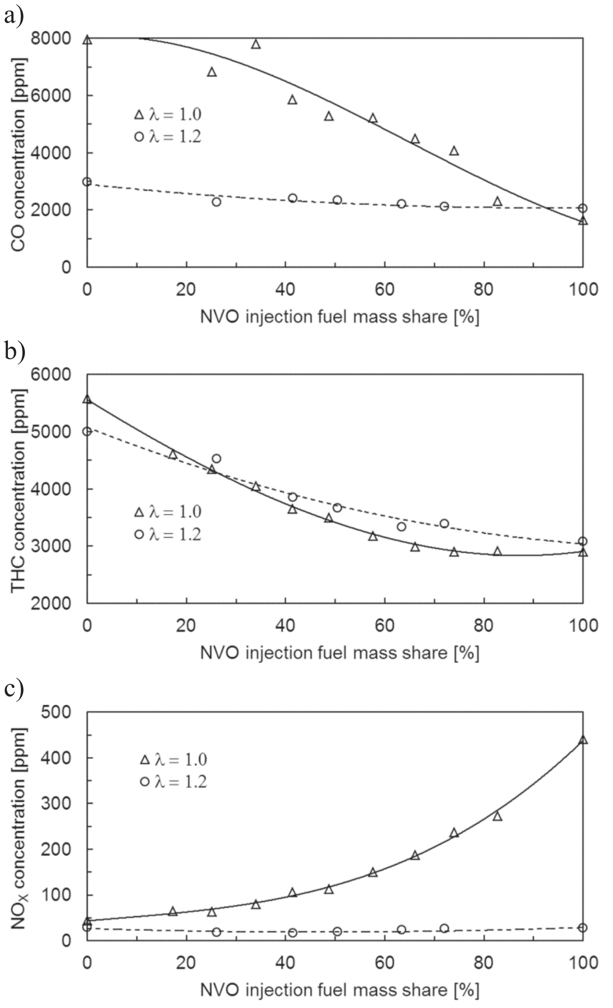


Fig. 6. Concentrations of regulated toxic components in exhaust gas with respect to NVO injection fuel mass share.

the THC content does not depend on mixture strength, yet it is approximately doubled for late injection when compared to early injection. In terms of emission index, unburned hydrocarbons constituted between 1.9% and 4% of the injected fuel. It should be noted that these relatively high HC levels were caused by the impact of wall-side effect at low temperatures inside the combustion chamber. The previous studies [25, 35] showed that early NVO injection of fuel modifies its chemical composition to a high extent. For this reason, it is expected that the fractional composition of unburned hydrocarbons will be altered, too. A detailed hydrocarbon speciation analysis is presented in the subsequent subsection of this paper.

The NO_X emission curves are shown in Fig. 6c. Although the FTIR detects different NO_X species, they will not be discussed here in detail. Let it suffice to say that they are mainly composed of NO under all investigated conditions. In the lean mixture regime, we can observe very low NO_X concentrations for all fuel injection strategies applied. The minimal NO_X concentration achieved for a lean mixture was approximately 15 ppm, which resulted in an indicated specific emission of 0.1 g/kW h. For a stoichiometric mixture and all fuel injected during NVO, the specific emission was as high as 1.66 g/kW h. However, it should be noted that the emission can be reduced to 0.2 g/kWh by retarding injection. A comparison of Figs. 6a and b reveals a trade-off between emissions of NO_X and CO in the case of a stoichiometric mixture. This can be attributed to a degree of mixture stratification. When the entire fuel was injected early in the NVO period, the mixture was perfectly homogeneous and, thus, oxygen was easily available in the combustible mixture. When more fuel was injected late, a higher degree of stratification was achieved, leading to an increase in CO emission and a decrease in NO_X emissions. In a stratified mixture, under overall stoichiometric conditions, combustion was initiated in higher temperature regions, usually the lean ones due to a lower fuel vaporization effect. At the highest heat release rate, when the temperature reaches its maximum, reactions are moved to colder and rich zones, where the conditions for NO production are less favourable. Additionally, the heat of vaporization of the NVO fuel reduced the temperature of the NVO gas, thus improving volumetric efficiency. As a result, more fuel was injected to maintain λ constant.

Consideration of Hydrocarbon Species

Exhaust-fuel reactions that take place during the NVO break long-chained hydrocarbons and produce methane, light unsaturated hydrocarbons, and aldehydes. It is therefore plausible that changes in fuel composition alter the structure of exhaust hydrocarbons. This issue is very important because some products of exhaust-fuel NVO reactions have very harmful effects. Another aspect worth considering relates to poor performance of a 3-way catalytic converter at low exhaust temperatures typical of HCCI engines [11].

Methane is one of the products of NVO fuel reactions. Its content in the combustible mixture varied from approx. 150 ppm at whole fuel injected during the main event compression to 2,000 ppm for whole fuel injected during NVO, regardless of mixture strength [35]. At its highest concentrations, CH_4 constituted up to 10% of all hydrocarbons. Fig. 7 shows that the trends in CH_4 concentration in the exhaust gas depends on mixture strength. In general, the ranges of variability are nearly the same for both values of l. At stoichiometric mixture, however, the increase in NVO fuel led to a decrease in CH_4 concentrations; at lean mixture, this trend was opposite. The observed effects can be attributed to the in-cylinder temperatures and differences in combustion evolutions under investigated conditions. For a stoichiometric mixture and late injection during compression, CH_4 is produced as a result of fuel reactions prior to combustion. At high quantities of NVO fuel, high amounts of CH_4 are produced during the NVO period. However, this hydrocarbon is consumed during the main combustion. As a result, the CH_4 concentrations are correlated with the THC concentrations and constitute approx. 5% of THC on a mass basis. In the lean mixture regime, the CH_4 concentration in exhaust gas increased with an increase in NVO fuel share. The maximum share of CH_4 in THC was as high as 10%. The reason for this emission trend was a lower combustion temperature. CH_4 produced during the NVO period was not oxygenated completely due to its higher auto-ignition temperature.

Methane poses a challenge from the point of view of exhaust after-treatment in a three-way catalytic converter. The light-off (50% conversion) temperature of CH_4 is approximately 800 K [36], while the exhaust temperature

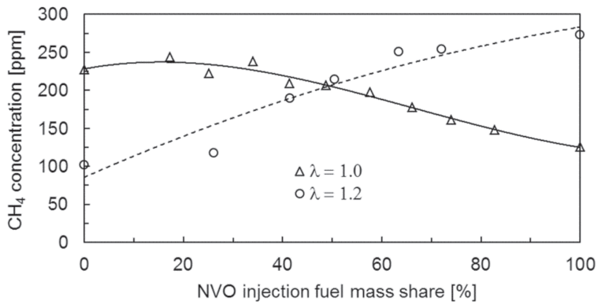


Fig. 7. Concentrations of CH_4 in exhaust gas with respect to NVO injection fuel mass share.

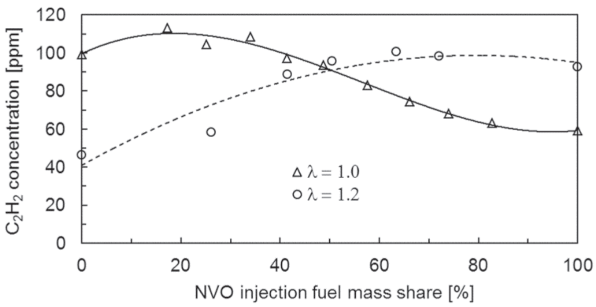
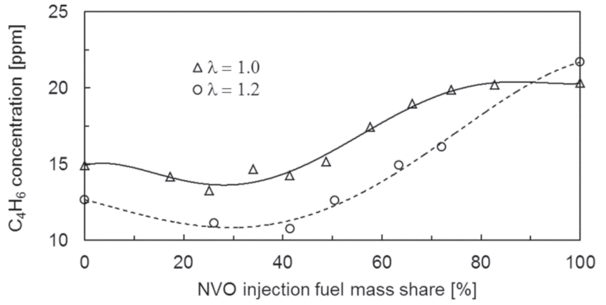


Fig. 8. Concentrations of C_2H_4 in exhaust gas with respect to NVO injection fuel mass share.



Fig, 9. Concentrations of C_4H_6 in exhaust gas with respect to NVO injection fuel mass share.

measured in the experiments at the exhaust runner varied from 620 K to 790 K. Thus, the cylinder-out emissions of this component can be treated as tailpipe emissions. Excessive emissions of CH_4 are problematic due to its greenhouse effect.

Similarly to CH_4, acetylene emissions exhibit different responses to injection strategies for different mixture strengths (Fig. 8). Produced by exhaust-fuel reactions during the NVO period, acetylene is one of the most effective products in terms of improving auto-ignition properties. Its content in the combustible mixture was varied approximately between 600 ppm and 50 ppm, regardless of air excess. From the point of view of exhaust after-treatment, C_2H_2 is important due to its inhibiting effect.

Among different hydrocarbons emitted by combustion processes, 1,3-butadiene is of the highest importance due to its carcinogenic potential. A concentration of C_4H_6 in the ambient air even as low as 2 ppm is regarded as dangerous [5]. It should be noted that C_4H_6 is considered by the U.S. Environmental Protection Agency as the most harmful of all toxic compounds emitted by motor vehicles [37, 38]. 1,3-butadiene concentrations moderately increase when more fuel is injected during the NVO period, regardless of l. The results given in Fig. 9 demonstrate that emissions can be reduced for split fuel injection.

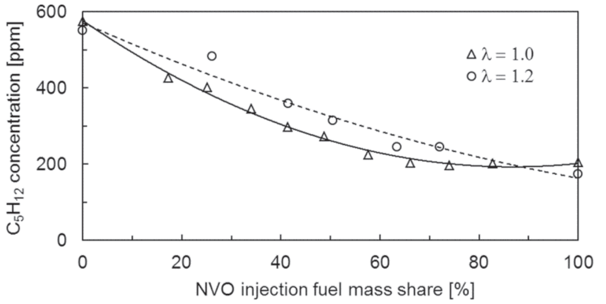


Fig. 10. Concentrations of C_5H_{12} in exhaust gas with respect to NVO injection fuel mass share.

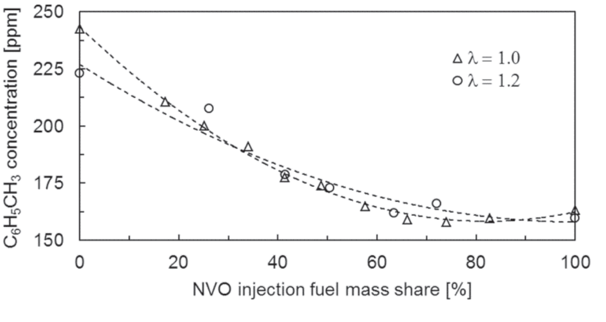


Fig. 11. Concentrations of aromatics in exhaust gas with respect to NVO injection fuel mass share.

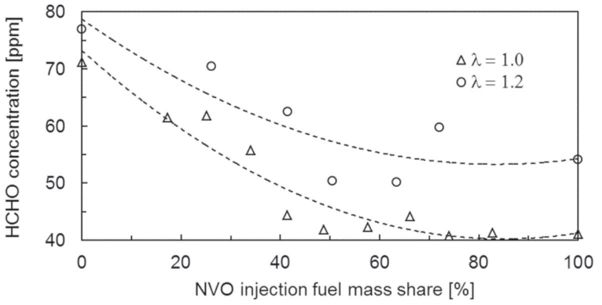


Fig. 12. Concentrations of HCHO in exhaust gas with respect to NVO injection fuel mass share.

Under the investigated conditions, the emissions of heavier hydrocarbons detected by the FTIR analyser, i.e. pentane (total of n-pentane and iso-pentane) and toluene (which represented all aromatics in FTIR measurements), reveal an opposite trend to that of lighter hydrocarbons, as can be seen in Figs 10 and 11. The increase in NVO fuel quantity reduces emissions of the aforementioned hydrocarbons. The pentanes content was reduced by a factor of three, while the content of aromatics dropped by 30% relative. The trade-off between light and heavy hydrocarbons for the two applied injection strategies was the same as the changes in fuel composition observed after NVO.

It is also worth drawing attention to the results of oxygenated hydrocarbon emissions. Among them, after C_4H_6, formaldehyde is the second most harmful gas emitted by motor vehicles [6]. It should be noted that high production of this compound was identified as a result of exhaust-fuel reactions during the NVO period. However, it has been found that increase in the NVO fuel share reduces HCHO concentrations, as shown in Fig. 12.

Conclusions

This study investigated the problem of emissions in a gasoline-fuelled HCCI engine. To induce HCCI combustion, the NVO technique was applied. The engine was run at two fuelling rates providing stoichiometric and lean ($\lambda = 1.2$) mixtures. Variable injection strategies were applied where the fuel dose was split between all fuel injected early during NVO and all fuel injected during the main event. The detailed speciation analysis of hydrocarbon emissions was performed to provide comprehensive data on the effects of injection strategies. The results of the study can be summarized as follows:

1. The choice of an injection strategy has great impact on the composition of hydrocarbons from residually affected HCCI engines.
2. The increase in fraction of the fuel injected during exhaust compression increases emission of 1,3-butediene to approximately 20 ppm, regardless of excess air ratio. In contrast, the concentration of formaldehyde decreases under the same conditions. The emissions of these harmful hydrocarbons should be taken into consideration in processes of control algorithm designs.
3. Emissions of methane can be approximately doubled by varying the injection strategy. However, the trend depends on excess air ratio. For a stoichiometric mixture, the increase in the NVO fuel reduces emission, while for a lean mixture the emission is higher. The same trend applies to acetylene.
4. High emissions of methane in raw exhaust can be problematic from the point of view of performance of a three-way catalytic converter. CH_4 has a high light-off temperature and thus cannot be removed from the exhaust in the catalytic converter in the low load regime of engine operation.
5. The application of early NVO injection reduces the emissions of pentanes by approximately 70% and of aromatics by approximately 30% when compared to all fuel injected during the main event.

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