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Lemel, Mikael; Hultqvist, Anders; Vressner, Andreas; Nordgren, Henrik; Persson, Håkan; Johansson, Bengt

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LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

Quantification of the Formaldehyde Emissions from Different HCCI Engines Running on a Range of Fuels

Mikael Lemel, Anders Hultqvist, Andreas Vressner, Henrik Nordgren,
Håkan Persson and Bengt Johansson

Div. of Combustion Engines, Department of Heat and Power Engineering Lund Institute of Technology

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ABSTRACT

In this paper, the formaldehyde emissions from three different types of homogenous charge compression ignition (HCCI) engines are quantified for a range of fuels by means of Fourier Transform Infra Red (FTIR) spectroscopic analysis. The engines types are differentiated in the way the charge is prepared. The characterized engines are; the conventional port fuel injected one, a type that traps residuals by means of a Negative Valve Overlap (NVO) and finally a Direct Injected (DI) one. Fuels ranging from pure n-heptane to iso-octane via diesel, gasoline, PRF80, methanol and ethanol were characterized.

Generally, the amount of formaldehyde found in the exhaust was decreasing with decreasing air/fuel ratio, advanced timing and increasing cycle temperature. It was found that increasing the source of formaldehyde i.e. the ratio of heat released in the cool-flame, brought on higher exhaust contents of formaldehyde. The application of a standard three-way catalyst completely removed formaldehyde from the exhaust stream.

INTRODUCTION

Over the last decade, the HCCI engine has shown a strong potential of realizing high efficiency in combination with low emissions for a range of fuels. However, many issues still have to be addressed and in previous works, questions have been raised on the presence of hazardous substances for our health, such as formaldehyde. Formaldehyde is a carcinogenic Aldehyde that isn't regulated as a single specie emission. However, it is indirectly limited by the restriction of the total hydrocarbon content in the exhaust.

The HCCI engine combines high efficiency with low nitric oxide (NO_x)- and soot emissions. The HCCI engine differs from the conventional engines since there isn't a

conventionally propagating flame. Reactions are more distributed and occur simultaneously throughout the combustion chamber. The low NO_x emissions are achieved because of low combustion temperatures due to a highly diluted mixture slowing down the chemistry and distributing the released heat in a larger mass. This is unfortunately also the reason why the emissions of carbon monoxide (CO) and hydrocarbons (HC) from the HCCI engine is highly sensitive to combustion timing. These emissions are likely to increase at low loads for the HCCI combustion since slower chemistry results in lower cycle temperatures.

Since the HCCI engine will emit unburned HC (UHC) there is also a risk that partially oxidized HC (so called oxygenated hydrocarbons, OHC) will be emitted. OHCs are a group of intermediates formed during the low temperature reactions. This group of species predominantly consists of formaldehyde, acetaldehyde, acraldehyde and formic acid. Concerning formaldehyde it is known that it is formed from decomposition of peroxy-alkyls, which is formed during slow oxygen addition at low temperatures [5]. This means that formaldehyde is formed slowly at the early combustion stages during the low temperature combustion, and that the maximum concentration value is reached just before the high temperature combustion initiates ($\cong 1100$ K). Somewhere after top dead center (TDC) the high temperature combustion starts to consume the formaldehyde in the bulk, rather rapidly. Furthermore, to avoid high concentrations of formaldehyde in the exhaust gas, a high combustion temperature should be sought for.

Investigations by Dec and Sjöberg [1,2,3], targeting the effect of bulk quenching by means of single zone modeling and experiments on a real engine suggested that OHCs might be present in the exhaust for HCCI combustion. The results from the single zone model, ideal for bulk reaction studies since it neglects heat

transfer losses and therefore also the crevice and near-wall effects, pointed out a lean load limit, where CO emissions increased rapidly, followed by a more moderate increase of HC and OHC. The experiments performed by the authors above were done at correspondent conditions to strengthen the results for the single zone model. To acquire the concentration of the OHC in the experimental part the authors above performed a carbon balance count, with the limitation not knowing what species being accounted for. Another drawback was that the flame ionization detector (FID) might have detected some of the OHCs, resulting in a too high net value of UHCs and too low net value OHCs.

Formaldehyde (CHOH) is an indicator of the onset of the cool combustion process. Therefore formaldehyde concentrations have been imaged with laser induced fluorescence (LIF) to acquire better knowledge of where the combustion process is initiated. During some of these measurements [4], some interesting observations were made under typical HCCI conditions. As expected formaldehyde started showing up some 20 crank angle degrees (CADs) before top dead center (BTDC) when the cool flame went off. When the high temperature regime then was initiated, close after TDC, the formaldehyde was completely consumed 10–15 CADs later. Further down in the expansion stroke, somewhere around 50 CAD ATDC, the formaldehyde signal surprisingly appeared again. If the signal in fact is from formaldehyde some explanations could be given. One theory is that some part of the HC that was pressed down in the crevice volumes during the high temperature regime slips out in the bulk volume later in the expansion stroke when the temperature and pressure is lower and more favorable for intermediate forming. Another theory is that OHC is pressed down in crevices by the compression, in the same way as UHC, and then slips out in bulk during expansion. Most likely is perhaps a combination of the both reasons given.

Because of these previous investigations, the intentions in this work are to;

- Quantify the formaldehyde exhaust concentration.
- Indicate if bulk quenching effects is an issue for the formaldehyde emissions.
- Indicate if there is a base contribution of formaldehyde from crevices and near wall regions.
- Investigate how the fuel type influences the formaldehyde emission level.
- Investigate how the formaldehyde emissions level changes by increasing the source of formaldehyde, i.e. “cool flame”.
- Investigate how large influence the cycle top temperature has on exhaust formaldehyde levels.

EXPERIMENTAL SETUP

The experiments in this work were conducted on three different HCCI engines.

Firstly- the exhausts were analyzed from a HCCI engine with port fuel injection. This engine is a Scania D12 modified for single cylinder operation with port fuel injection and preheating of the intake air. Three different, flat, piston crowns with different compression ratios were used, enabling investigations of the fuels in Table 1. For all runs, except for the timing sweeps, the combustion timing was kept constant by changing the intake air temperature. Inlet pressure was kept at 1 bar(a) and the engine speed at 1200 rpm. Specific for this engine was a spacer placed between the engine body and the cylinder head with the purpose of allowing ion current sensing. All other specifications regarding the engine were the same as in Table 3. Concerning this work, the sparkplug holes in the spacer increased the cylinder crevice volume significantly and most likely will this contribute to the OHC emissions.

Table 1 Fuels, compression ratios and CA50s for the port injected Scania D12 engine

| Fuel | RON | CA50% | Compression ratio |
|------------|-----|--------|-------------------|
| n-Heptane | 0 | 2 BTDC | 11.5:1 |
| Diesel | 30 | 2 BTDC | 11.5:1 |
| PRF80 | 80 | 1 ATDC | 16.7:1 |
| Gasoline | 95 | 1 ATDC | 16.7:1 |
| Iso-octane | 100 | 1 ATDC | 18:1 |
| Methanol | 106 | 1 ATDC | 18:1 |
| Ethanol | 107 | 1 ATDC | 18:1 |

**Diesel @RON 30 is equivalent to CN 52*

Secondly- the emissions were measured from a HCCI engine trapping residuals by means of negative valve overlapping (NVO). The NVO-engine is based on an in-line six-cylinder Volvo passenger car spark ignition engine. It has the possibility of spark assistance for widening the operational range and a cam phasing mechanism for changing the amount of trapped residuals, allowing control of the ignition timing. The fuel for all runs for this engine was gasoline as can be seen in Table 2.

Table 2 Engine data for the engine employing NVO

| | |
|------------------------------|----------------------|
| Displacement volume | 2922 cm ³ |
| Number of cylinders | 6 |
| Bore | 83 mm |
| Stroke | 90 mm |
| Compression ratio | 10.3:1 |
| Valve lift | 3 mm |
| Inlet/Exhaust valve duration | 150 CAD |
| Fuel | RON 98 |
| Water temperature | 95°C |
| Inlet temperature | 50°C |

The exhausts from all the six cylinders were mixed before measured with the possibility of collecting the exhaust before or after two standard three-way catalytic converters. The engine was fed a slightly lean air/fuel-mixture, $\lambda=1.08-1.12$ @ 1000 rpm and wide open throttle (WOT).

Lastly- the exhausts from a direct injected, single cylinder, HCCI engine were measured. In this modified Scania D12 early direct injection applied is between the limits in Table 3. In this case, the start of injection (SOI) and exhaust gas recirculation (EGR) were used to keep the combustion phasing constant while trying to minimize the NO_x , HC and CO emissions in the trade-off. The NO_x emissions were kept below 40 ppm for all runs by employing high levels of EGR.

Table 3 Engine data for the DI-engine

| | |
|--------------------------|----------------------|
| Displacement volume | 1951 cm ³ |
| Compression ratio | 12.8:1 |
| Bore | 127 mm |
| Stroke | 154 mm |
| Inlet valve open | 39° BTDC |
| Inlet valve close | 63° ABDC |
| Exhaust valve open | 82° BBDC |
| Exhaust valve close | 38° ATDC |
| Fuel 1 | Diesel CN 52 |
| Fuel 2 | Diesel CN 40 |
| Engine speed | 1200 rpm |
| Inlet temperature | ~20-25°C |
| Inlet pressure | 1-3 bar |
| Start of injection (SOI) | 60° to 5° BTDC |
| Common rail pressure | 1500 bar |
| EGR | 40 -70% |

For this engine two diesel fuels with different cetane numbers were used, together with two different swirl ratios and two different nozzles.

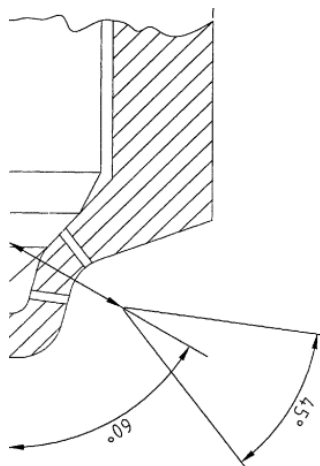


Figure 1 Sketch of the nozzle with colliding sprays [8]

The higher swirl ratio was achieved by covering one of the intake ports. The special nozzle realized colliding sprays according to Figure 1.

MEASUREMENT SYSTEM

Fourier Transform Infrared (FTIR) Spectrometry

An FTIR spectrometer was used in the experiments to acquire the absorption spectra for the exhausts. The FTIR works by the principal of matching reference spectra of the anticipated components against the exhaust sample spectrum. By using multipliers the effort is to subtract the reference spectra from the sample spectra to get a zero residual. If this is successful, the concentration of the components is given as the concentration of the reference spectrum times the multiplier used in the subtraction.

The use of multipliers to achieve the concentrations is possible due to the Lambert-Bourgher-Beer law. This is the basic law of spectroscopic analysis [7] and it states that the absorbance is directly proportional to the concentration of the sample gas at a given wavelength. For this to be valid the optical pathway must be constant, but for a FTIR it is.

To avoid unnecessary condensation of hydrocarbons and damage to the FTIR detector cell, the exhausts are heated and hence water vapor is present in the sample. Unfortunately water vapor absorbs at almost every frequency, clouding trace components such as formaldehyde. Therefore new water spectra were acquired before performing the analysis so that the fingerprint of water vapor was as exact as possible. See Figure 4 for reference. Additionally, new spectra of concentrations of 40- and 200 ppm formaldehyde were created as well. Still the water vapor peaks governed the choice of evaluation area of formaldehyde. Many different settings and areas were tried with the aim of minimizing the residuals shown in Figure 3.

Concerning the choice of evaluation interval for formaldehyde, basically three different setting were tested. For understanding these see

Figure 2 to Figure 4.

1. 1650-1850 cm⁻¹, with water as a major interfering component (among others)
2. 2650-2850 cm⁻¹, with only the fuel hydrocarbon and acetaldehyde as interfering components
3. 2650-2850 cm⁻¹, as above but including water vapor as a interfering component

In general the first alternative gave quite high values of formaldehyde, but with unacceptable high residuals for most cases. The second alternative showed acceptable values with acceptable residuals but most often discontinuities were present in the results. The third alternative gave trustworthy values with the lowest residuals (<0.005, acceptable is <0.02) for all cases. Therefore alternative 3 was chosen which can be seen in Table 4.

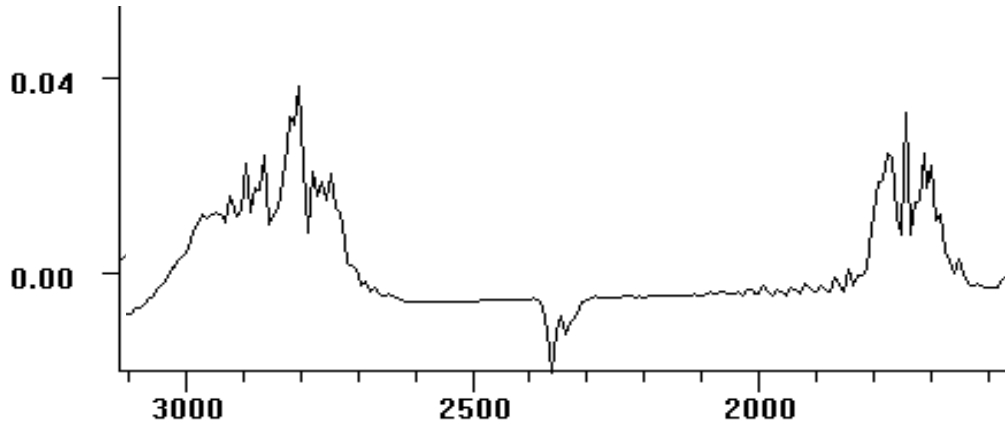


Figure 2 A calibration spectrum on formaldehyde of about 200 ppm. The spectrum was specifically acquired for the FTIR analysis performed in this work.

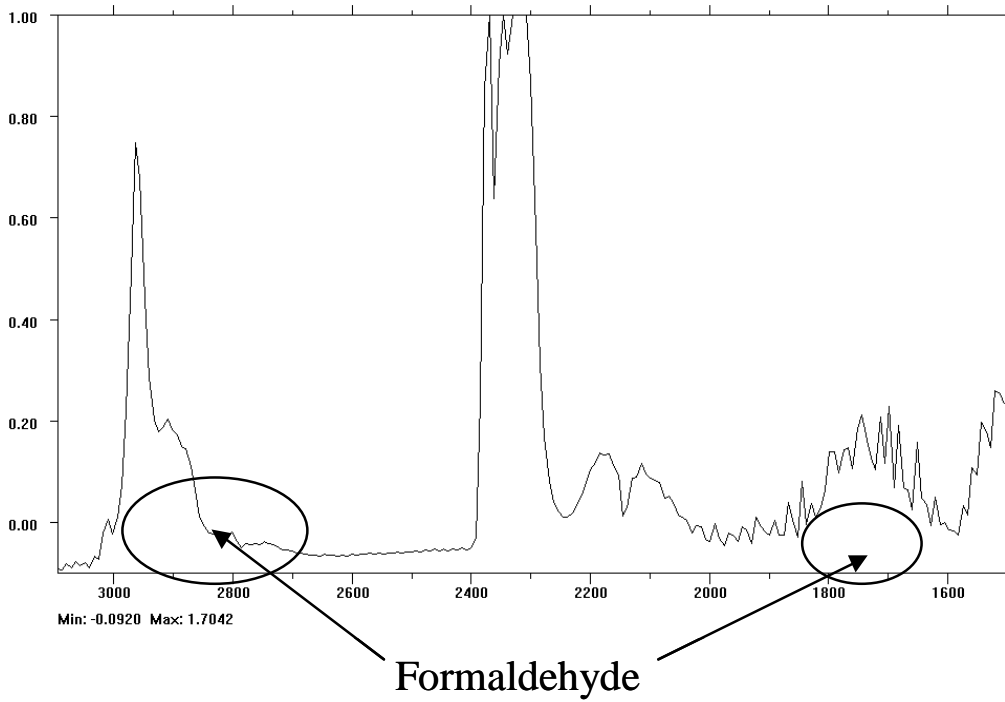


Figure 3 A sample spectrum from a run with *n*-heptane at $\lambda=6$, $CA50\approx 1^\circ$ ATDC and $T_{in}=135^\circ\text{C}$. The circled areas illustrates where formaldehyde absorbs and that formaldehyde truly is a trace component.

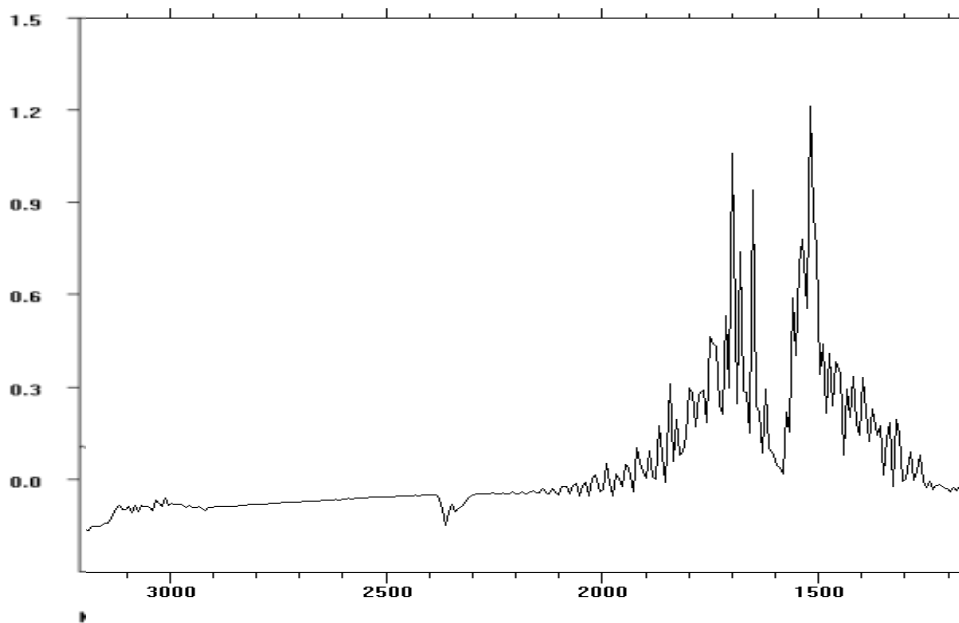


Figure 4 A calibration water vapor spectrum @ 6 %. Specifically acquired for this FTIR analysis.

Table 4 The settings used in the analysis

Basic Evaluation Settings

| Component | Intervall 1 | Intervall 2 | Intervall 3 | Interferring components | Absorbtion limit |
|--------------|-------------|-------------|-------------|--|------------------|
| H2O | 1810-1984 | | | CO,CO2,NO,formaldehyde,acetaldehyde,(HCfuel*) | 1.0 |
| CO | 2014-2235 | | | H2O,CO2,N2O,NO,NO2,(HCfuel**) | 0.5 |
| CO2 | 2014-2223 | | | H2O,CO,N2O,NO,NO2,(HCfuel**) | 3.0 |
| N2O | 2045-2223 | | | H2O,CO,CO2,NO,NO2,HCfuel*) | 0.5 |
| NO (CF=0,9) | 1810-1984 | 2500-2520 | | H2O,N2O,formaldehyde,acetaldehyde, (HCfuel*) | 0.8;1.0 |
| NO2 (CF=0,5) | 1200-1220 | 1567-1644 | 1976-2014 | H2O,CO,CH4,NO,formaldehyde,acetaldehyde,HCfuel | 0.5;0.8;05 |
| Formaldehyde | 2650-2850 | | | H2O,acetaldehyde, HCfuel | 0.5 |
| Acetaldehyde | 2650-2850 | | | H2O,formaldehyde,HCfuel | 0.5 |

*denotes the runs for methanol, ethanol or toluen (from gasoline), ** denotes only the runs for methanol

Specific for each fuel component

| Component | Intervall | relevant information | Interferring components | Absorbtion limit |
|------------|-----------|----------------------|--|------------------|
| n-Heptane | 2817-3018 | also used for diesel | H2O,CH4,NO2,formaldehyde,acetaldehyde | 0,8 |
| Iso-octane | 2817-3018 | | H2O,CH4,NO2,formaldehyde,acetaldehyde | 0,5 |
| Ethanol | 2748-3049 | | H2O,CH4,NO2,formaldehyde,acetaldehyde | 1,0 |
| Methanol | 2779-3095 | | H2O,formaldehyde,acetaldehyde | (1,0) |
| Toluen | 1810-1976 | used for gasoline | H2O,CH4,NO,xylenes,formaldehyde,acetaldehyde | 1,0 |
| P-xylen | 2600-2800 | used for gasoline | H2O,CH4,o-xylene,formaldehyde,acetaldehyde | 1,0 |

Since the experiment had included several different fuels with and without cool flame characteristics, the main intention became to perform a fair comparison between all the fuels. Therefore it was decided to evaluate the formaldehyde in the exact same region for all the runs, merely adding the interfering hydrocarbons in the formaldehyde evaluation for each fuel. The settings for the standard combustion products (H₂O, CO, CO₂, NO, NO₂), were suggested by a specialist at the Danish emission reduction company, Haldor Topsøe A/S.

In Table 4, the final settings are illustrated. Typically all hydrocarbons absorb in $3000 \pm 200 \text{ cm}^{-1}$ meaning they

will always interfere with the formaldehyde peaks. Additionally fuels with OH- groups (methanol, ethanol), tend to absorb in much wider areas interfering with almost all other components, very similar to water vapor.

The FTIR measures specific components and can only measure components that exist as a reference spectra in the software, some difficulties emerged for the evaluation of the two real fuels. These fuel's constituents are largely unknown and are therefore unsuited for FTIR evaluation. For the diesel runs, n-heptane was used as a supplement and for the gasoline runs, toluene and p-

xylylene were used. The diesel supplement gave acceptable residuals for most cases while the residuals for the gasoline case were too high. For both of these fuels the focus should be on the trends and not on the amounts. If there were any error estimates, they would be $\pm 30\%$ of the measured value for the diesel case while for the gasoline case the measurement is so doubtful an error estimate makes no sense.

Additionally, not all unburned HC is in the form of the original fuel, meaning that many different hydrocarbons may be present in the exhausts even for the single component fuels. This could make the evaluation less trustworthy, but nevertheless the formaldehyde residuals were acceptable in all cases with single component fuels.

Due to the lack of reference files for other OHC species, only formaldehyde and acetaldehyde could be evaluated. As pointed out earlier, these two absorb in the same region. To get an estimate of the total amount of OHC, the sum of these two were added up in the following way; $OHC = \text{formaldehyde} + 2 * \text{acetaldehyde}$ (since acetaldehyde has two carbon atoms).

For the formaldehyde measurements the general measurement error is estimated to $\pm 20\%$ of the absolute measured value. During the same measurement sequence, the repeatability lies within $\pm 2\%$ of the measured value.

FTIR specifications

- Resolution = 8 cm^{-1} (fixed)
- Scanning frequency = $2 * 5 \text{ Hz}$ (fixed)
- The sampling time was set to 20 s (for the calibrations 60 s)
- Optical pathway = 2.00 m (fixed)
- Heated sample cell and sample lines (180° C) -> emissions measured "wet"
- Scanning interval $[900-4500] \text{ cm}^{-1}$

The scanning frequency and the sample time results in that the infrared radiation sweeps each sample 200 times per measuring point. These sweeps are averaged and therefore the sample spectra are relatively insensitive to variations in the exhaust mixture and pressure fluctuations.

RESULTS AND DISCUSSION

Port fuel injected HCCI

In Figure 5, the formaldehyde concentration in the exhaust for three load sweeps for methanol, ethanol and iso-octane is showed. The formaldehyde concentration

is rather constant for $\lambda < 4$. For $\lambda > 4$, a quite high increase is noticeable for all fuels. This result seems to agree with the lean limit suggested by Dec et al [1,2,3].

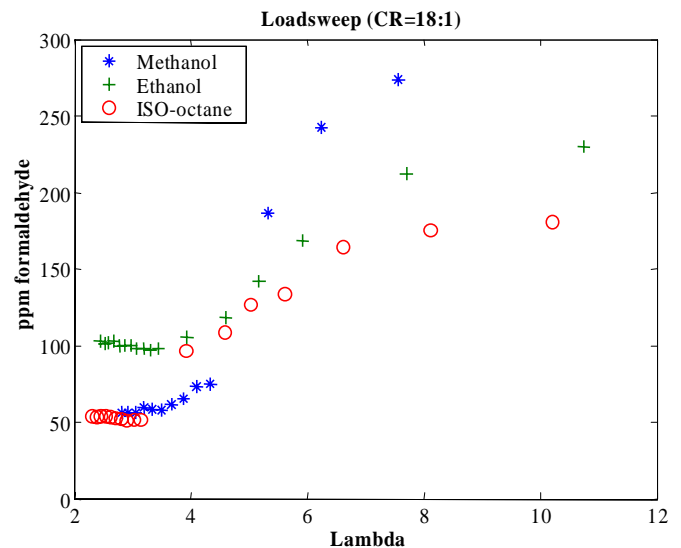


Figure 5 The formaldehyde in the exhaust for three different fuels at the same compression ratio and combustion phasing.

It seems, as bulk effects also are present for OHC, such as formaldehyde. When looking at the CO emissions for the iso-octane case, a breakpoint could be observed already at $\lambda \sim 3$ (Figure 7). Probably for the richer cases ($\lambda < 4$) all the formaldehyde formed before the high temperature regime will be consumed if present in the bulk volume, and hence the formaldehyde left must origin from crevice or near-wall preserved hydrocarbons that is transformed into formaldehyde in the later part of the expansion stroke. Furthermore, under higher load conditions the bulk may be hot enough so as to promote the oxidation of formaldehyde emanating from crevices during the expansion stroke.

In Figure 6 load sweeps for gasoline, diesel and n-heptane are showed. The formaldehyde concentration for the runs with the two real fuels is a bit uncertain as discussed earlier. For the n-heptane case the breakpoint is not that clear as for the fuels in the previous figure.

The formaldehyde emissions in Figure 6 increases slowly (with λ) compared to the results in Figure 5, but it should be noted that the acetaldehyde (also an OHC species) concentration for the n-heptane run is quite high (80-120 ppm). This is of importance since acetaldehyde absorbs in the same region as formaldehyde.

In Figure 7 the CO emissions for the iso-octane and n-heptane runs are compared. For n-heptane, the CO emissions is almost the double compared to the run with iso-octane and begins to rise rapidly for $\lambda > 3.6$.

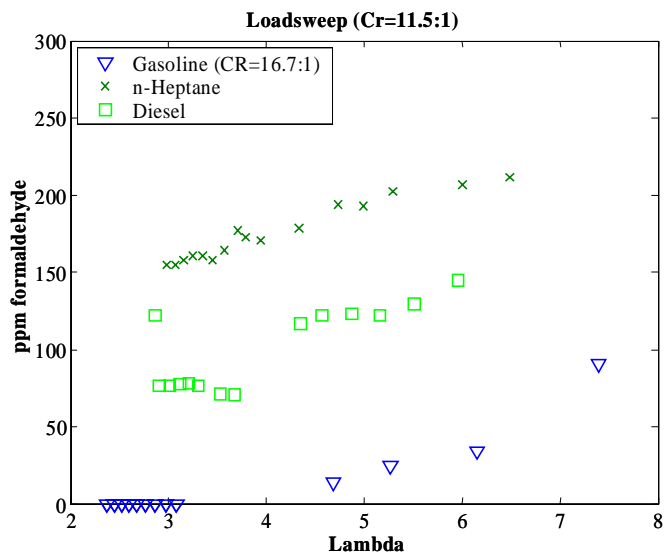


Figure 6 The formaldehyde emissions for Diesel and n-heptane at the lower compression ratio, CA50@2° BTDC. Gasoline at CR= 16.7 and CA50@1° ATDC.

It appears that n-heptane runs suffer from poorer combustion efficiency already at richer limits than for example iso-octane.

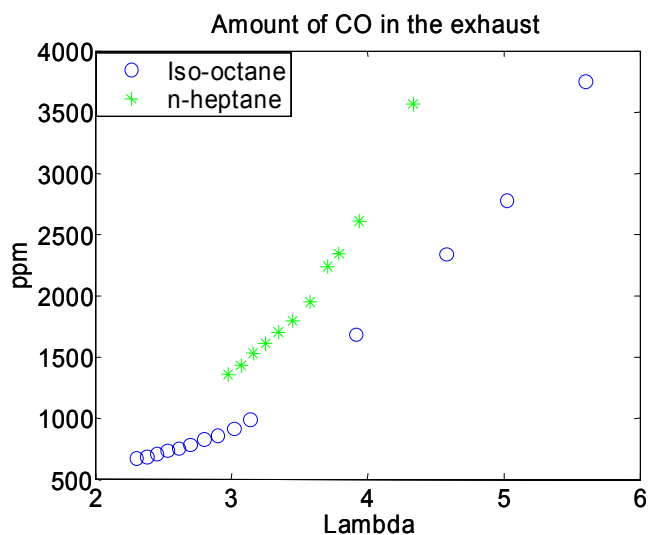


Figure 7 Exhaust CO concentrations for the n-heptane and iso-octane runs in the two previous figures.

This might be the explanation for the higher concentration of OHC for the n-heptane case at lower loads. Another, perhaps more likely, explanation is that higher, post cool flame, formaldehyde concentrations is brought on by the pronounced cool flame. This means that there is more formaldehyde to be consumed when the high temperature regime is initiated and if the high temperature energy release is small, the consumption of formaldehyde will only be partial and the emissions high. Additionally, the higher CO in the n-heptane case is likely due to the lower average cycle temperature.

In Figure 8, the OHC (here estimated as; OHC = formaldehyde + 2 * acetaldehyde) concentration is shown for a load sweep at constant EGR rate for all fuels. The fuels with lower RON number and with cool flame characteristics are clearly emitting higher contents of OHCs in the exhausts. This is quite expected since formaldehyde is formed in low temperature reactions and for cool flame fuels there is more time at these conditions. Furthermore, fuels with lower octane number, in general has a lower combustion temperature, resulting in a slower consumption of formaldehyde.

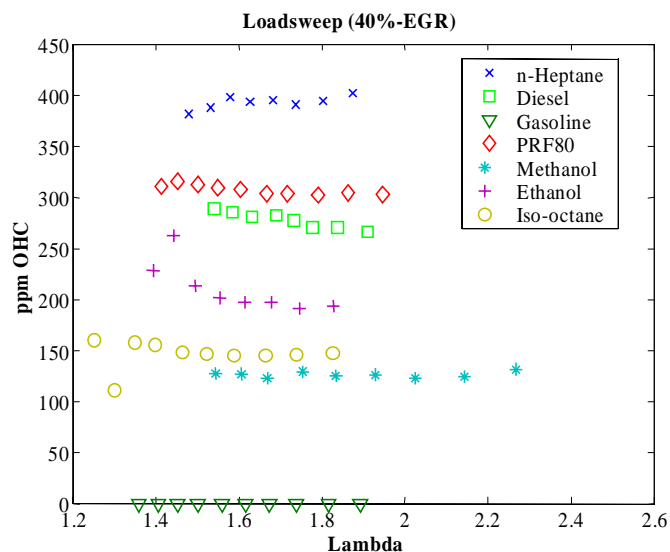


Figure 8 The OHC concentration in the exhausts for all fuels. See Table 1 for operating conditions.

In Figure 9, the effect of EGR on formaldehyde emissions are shown.

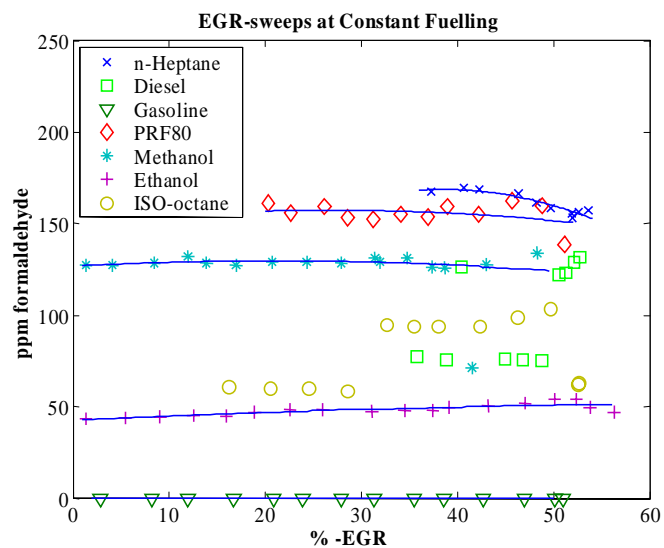


Figure 9 The formaldehyde concentration in the exhausts for all fuels.

There are some discontinuities for the results from the iso-octane and diesel runs. The main reason for the discontinuities is poorly subtraction of the HC species with a direct impact on the formaldehyde result. Still the most important result here is the weak effect that EGR rate has on the formaldehyde emissions.

For iso-octane, n-heptane and diesel for the port injected HCCI engine timing sweeps were also performed. To acquire the change in combustion phasing, constant fuelling @ $\lambda=3.0$ while changing the intake temperature was used. In Figure 10 the result is shown. For all the fuels, the formaldehyde concentration increase with retarded combustion phasing. This is expected due to the lower combustion temperature a retardation of the combustion phasing brings. The increase is strongest for the n-heptane case and this is probably coupled to the low temperature reactions.

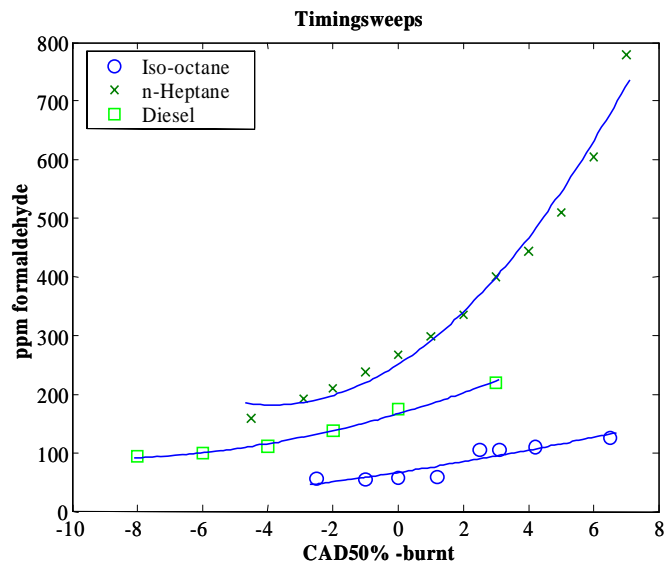


Figure 10 The formaldehyde concentration in the exhaust during a timing sweep for three fuels.

To investigate the influence of the low temperature reactions on the formaldehyde emissions, a heat release analysis was done for the n-heptane data in Figure 10. The results from the heat release calculations are shown in Figure 11 and Figure 12. In the first of them the formaldehyde concentration is plotted against the ratio of heat released in low temperature reactions, i.e. during the cool flame period (HRLow) to the total heat released (HRTot).

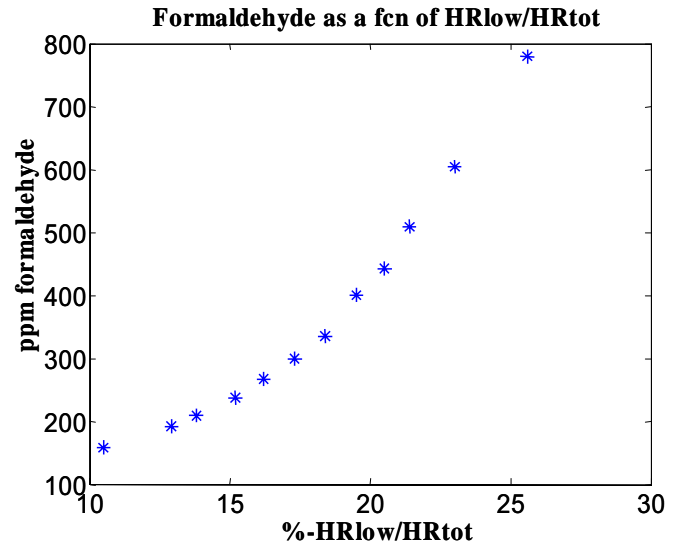


Figure 11 The formaldehyde concentration when displayed against the ratio of heat released in low temperature reactions to total heat released. The data is the n-heptane timing sweep.

When retarding the combustion phasing the HRLow-term increases moderately while the HRTot-term decreases more rapidly. This results in the total increase in the ratio HRLow/HRTot. It is clear that the formaldehyde concentration is strongly dependent of this ratio. The reason is twofold with an increase of the formaldehyde source (HRLow) and a decrease of the consumption term (HRTot).

In Figure 12 are the n-heptane data plotted against the cycle top temperature. The formaldehyde concentration is strongly coupled to the maximum cycle temperature. It seems as the curve approaches two asymptotes. The first is the temperature required for start of consumption of the formaldehyde in the bulk.

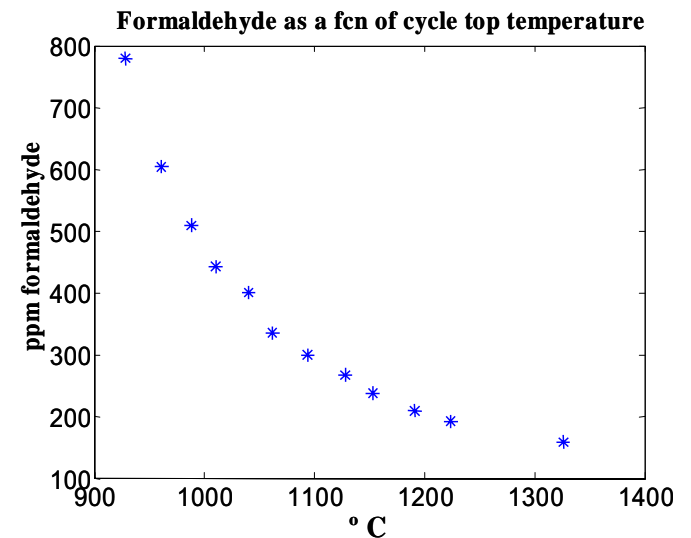


Figure 12 The formaldehyde concentration when displayed against the cycle top temperature for the n-heptane timing sweep data.

This temperature seems to be somewhere close, or just below 900 °C. This temperature corresponds quite well with the onset temperature of the high temperature reactions. The second asymptote is the amount of formaldehyde being left in the exhaust when the temperature is high enough for fully completed bulk reactions. This strengthens that there is a base contribution of formaldehyde caused by crevices and perhaps also by near wall regions.

Results- port injected HCCI with NVO

For the port injected HCCI with NVO, the fuel for all runs were gasoline. Due to the difficulties of evaluating this fuel with the FTIR technique (since the fuel's constituents are largely unknown), the only result reported here is the effect of the catalytic after treatment. The measured emissions after the catalyst is about 0~ppm, see Figure 13. Even though it has been stated earlier that the results from all gasoline runs are a bit tentative, the trend is clear.

Catalytical aftertreatment

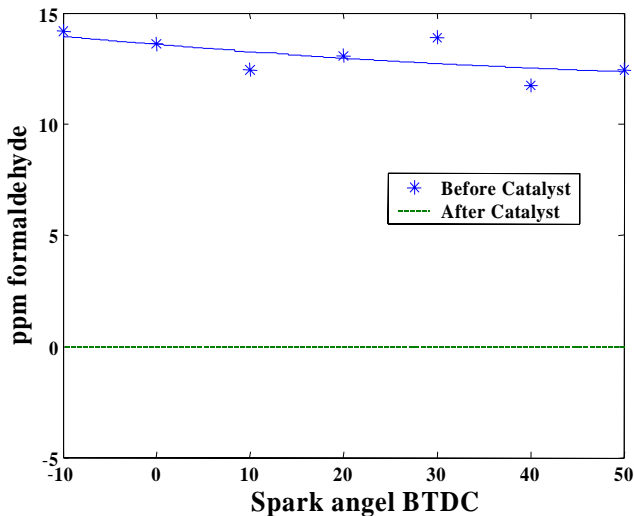


Figure 13 The formaldehyde concentration with and without catalytic after treatment. In this case the engine was run in spark assisted mode.

For verifying this, the two corresponding spectra were compared. In the area were both HC and OHC absorb ($2800\pm 100\text{ cm}^{-1}$), there was a clear reduction of absorption for the case with after treatment. Finally, the corresponding FID measurements showed about 10 ppm unburned HC in the exhaust. The 95% reduction of UHC supports the FTIR findings.

Results – direct injected HCCI

For the DI-engine basically two different types of load-sweeps were performed:

- Increasing the inlet pressure whilst keeping the λ -value constant ($\lambda=1$). Maintaining the CA50 timing around 7 ± 2 CADs ATDC by changing the start of injection (SOI) and EGR rate and also to keep the NO_x levels below 40-ppm.
- Inlet pressure constant and varying the λ -value by the fuel amount.

In Figure 14, the formaldehyde concentration is plotted against the IMEP and in Figure 15 against the inlet pressure. The formaldehyde concentration increase almost linearly with increasing inlet pressure and fuelling for all cases. This behavior is expected since an increase in injected fuel mass means that more fuel needs to be mixed before burning in the high temperature regime. Additionally, fuels with a higher Cetane number (CN) leave higher levels of formaldehyde in the exhaust, due to less time to mix before burning.

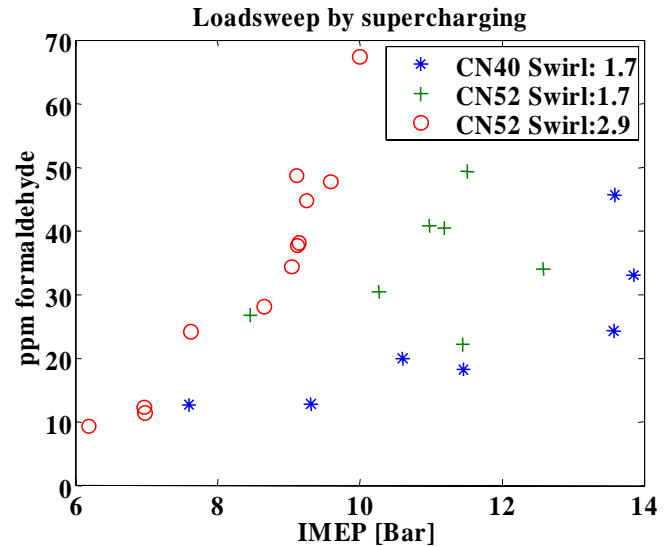


Figure 14 The formaldehyde emissions for a load sweep with two diesel fuels and two swirl ratios. Standard nozzle and $\lambda=1$.

Only a small influence of the swirl ratio could be observed. Emissions of formaldehyde are somewhat lower with a higher swirl at a given load. However, for a given boost level there is no difference, indicating higher combustion efficiency at higher swirl. The higher efficiency must be due to increased late cycle mixing, leading to better air utilization, considering the average air/fuel excess ratio being close to stoichiometric.

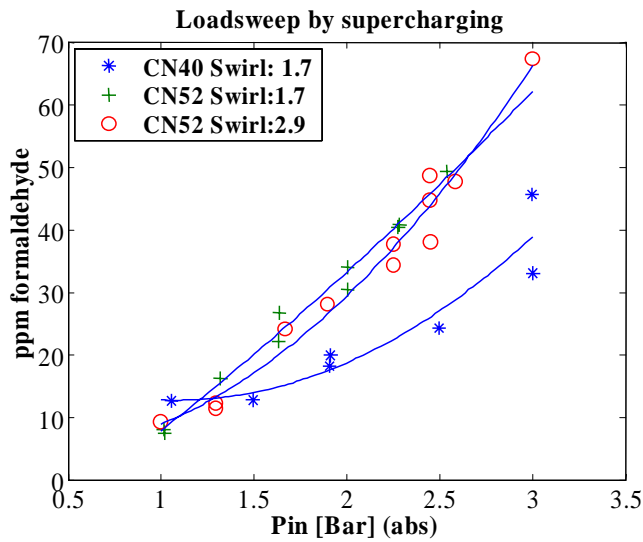


Figure 15 The formaldehyde emissions for a load sweep with two diesel fuels and two swirl ratios. Standard nozzle $\lambda \sim 1$.

The load-sweep by changing air/fuel excess ration is shown in Figure 16. Here three runs with diesel CN 52 and one run with diesel CN 40 are gathered. Some different inlet pressures (abs) were used as well as the nozzle with colliding sprays here referred to as nozzle 2 (Figure 1). Firstly, no clear difference between the two nozzles could be observed. What's really against all earlier results is the case with $P_{in}=3$ bar.

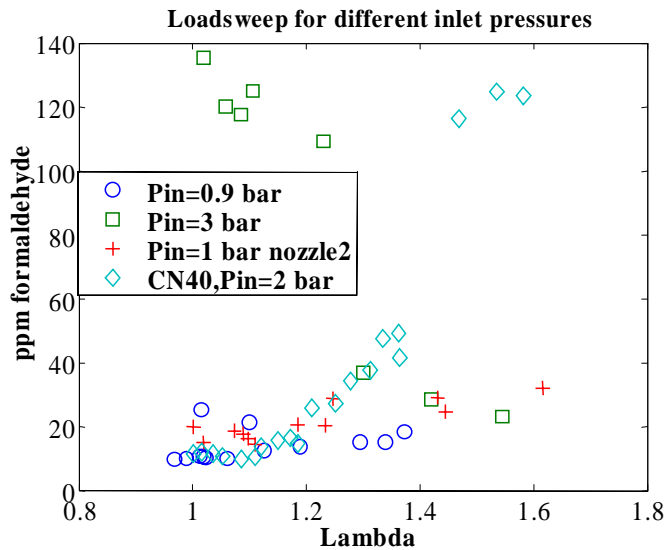


Figure 16 The formaldehyde concentration for a load sweep by changing fuelling. Intake pressure constant, only the low swirl ratio, both nozzles tested.

If this case is compared to the more expected one (see Table 5) with CN40 and $P_{in}=2$ bar some conclusions can be drawn. The results for $1 < \lambda < 1.25$ should give quite low HC and OHC emission levels if the mixture had enough mixing time. This has been shown for the other engine results. What differs for the $P_{in}=3$ bar case is actually the

SOI, that is around 10 CADs later compared to the $P_{in}=2$ bar. This could lead to an increased sensibility in the sense of more inhomogeneous zones producing more HC and OHC. When λ is increased the SOI is retarded to maintain the CA50 timing, which in this case should lead to more inhomogeneous mixture, which can be seen for the CN40 case. But the $P_{in}=3$ bar case doesn't show this trend. Factors that can be the explanation here is; problem with vaporization of the fuel, dilution and poor mixing.

Table 5 Data comparing the two opposite trends in Figure 16

| | CN52 | CN40 |
|-----------------|-------------|-------------|
| Pin | 3,0 bar | 2,0 bar |
| CA50 cad ATDC | 7,5±0,5 | 7,5±0,5 |
| EGR | 70% | 55-60% |
| SOI (lamda=1) | 27 cad BTDC | 36 cad BTDC |
| SOI (lamda=1,5) | 20 cad BTDC | 29 cad BTDC |
| HC | <3000 ppm | <1000 ppm |
| Nox | ~0 ppm | ~5 ppm |
| Tin | ~35°C | ~23°C |
| nozzle | std | std |

SUMMARY AND CONCLUSIONS

FTIR measurements of formaldehyde were performed on three different HCCI engines applying; port fuel injection, negative valve overlap and direct injection.

It was found that the FTIR analysis of exhaust from real fuels is cumbersome since their specific constituents and interfering species are largely unknown.

When the FTIR technique is applied to the exhaust from the well defined fuels, the analysis is trustworthy with errors within the range of $\pm 20\%$ of the absolute measured value.

Formaldehyde exists in the exhausts of all the tested HCCI engines. In general, fuels with stronger "cool flame" characteristic emit higher levels of formaldehyde. The reason is twofold; these fuels benefit the forming of formaldehyde due to the low temperature reactions, while the lower cycle temperature results in poorer consumption in the high temperature regime.

Cycle temperature has the strongest effect on the emission levels of formaldehyde. Parameters such as; λ , CA50, Cr, Pin and Tin, influencing the peak cycle temperature, affect of course the formaldehyde emissions as well.

For a constant CA50, the EGR-rate seemed to have no effect on the formaldehyde emissions due to similar combustion temperatures.

A lower temperature limit was found for the onset of consumption of formaldehyde in the bulk.

In port fuelled engines, there will always be a base contribution of formaldehyde due to crevices.

Catalytic after treatment with a standard 3-way catalyst at lambda just above 1, reduced the formaldehyde concentration to levels below the detection limit on the NVO-engine.

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REFERENCES

1. J.E. Dec and M. Sjöberg, "A Parametric Study of HCCI Combustion – the Source of Emissions at Low Loads and the Effects of GDI Fuel Injection," SAE Paper 2003-01-0752, 2003
2. J.E. Dec. "A Computational Study of the Effects of Low Fuel Loading and EGR on Heat Release Rates and Combustion Limits in HCCI Engines," SAE Paper 2002-01-1309, 2002.
3. M. Sjöberg. and J.E. Dec. "Combined Effects of Fuel-type and Engine Speed on Intake Temperature Requirements and Completeness of Bulk-gas for HCCI Combustion," SAE Paper 2003-01-3173, 2003
4. R. Collin et al. "Simultaneous OH- and formaldehyde-LIF measurements in an HCCI engine", SAE PAPER 2003-01-3218, 2003
5. P. Amnéus et al., "Formaldehyde and Hydroxyl Radicals in an HCCI Engine –Calculations and LIF-measurements,"
6. L-E. Åmand and C.J. Tullin. "The Theory Behind FTIR analysis", Dep. Of Energy Conversion, Chalmers University of Technology, Sweden,
7. Reference [6] referring to: Griffiths, P.R., de Haseth, J.A., "Fourier Transform Infrared Spectroscopy", Chemical Analysis, 83, John Wiley & Sons, 1986
8. H. Nordgren, A. Hultqvist and B. Johansson. "Start of injection strategies for HCCI-combustion" SAE Paper 2004-01-2990, 2004