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Combustion Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713456315>

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Per G. Kristensen^a; Bent Karll^a; Anders Broe Bendtsen^b; Peter Glarborg^b; Kim Dam-Johansen^b

^a Danish Gas Technology Centre, Horsholm, DK, Denmark ^b Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark

To cite this Article Kristensen, Per G. , Karll, Bent , Bendtsen, Anders Broe , Glarborg, Peter and Dam-Johansen, Kim(2000) 'Exhaust Oxidation of Unburned Hydrocarbons from Lean-Burn Natural Gas Engines', Combustion Science and Technology, 157: 1, 262 – 292

To link to this Article: DOI: 10.1080/00102200008947319

URL: <http://dx.doi.org/10.1080/00102200008947319>

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Exhaust Oxidation of Unburned Hydrocarbons from Lean-Burn Natural Gas Engines

PER G. KRISTENSEN^{a*}, BENT KARLL^{a*},
ANDERS BROE BENDTSEN^{b†}, PETER GLARBORG^{b†} and
KIM DAM-JOHANSEN^{b†}

^aDanish Gas Technology Centre DK-2870 Hørsholm, Denmark and ^bDepartment of Chemical Engineering, Technical University of Denmark, Building 229, 2800 Lyngby, Denmark

(Received July 06, 1999; In final form February 04, 2000)

Post cylinder oxidation of unburned hydrocarbons (UHC) was studied using a 35 kW test engine. The engine was equipped with an insulated exhaust reactor to extend the residence time. The exhaust reactor performance has been characterised under the basic engine operating conditions, and under conditions where temperature and composition (NO_x level) of the exhaust were modified independent of engine settings. The experiments studied spanned a wide range of moderately lean-burn conditions. The composition at the exhaust port was as follows: O_2 5–9% (engine excess air ratios of 1.28–1.75), UHC 1000–7000 ppm, CO 550 ppm, NO_x 0–1400 ppm. The temperature varied from 600 to 700°C. In addition, experiments with injection of hydrogen peroxide to promote UHC oxidation in the exhaust system were conducted.

The amount of UHC oxidised in the exhaust system depended closely on the exhaust temperature, residence time and concentration of nitrogen oxides in the exhaust gas. The increased reaction time in the exhaust reactor caused an oxidation of the exhaust hydrocarbons of up to 90% with CO as the major oxidation product, but the reactor efficiency decreased as the engine was operated at leaner conditions, due to lower temperatures and lower NO_x levels. Levels of nitrogen oxides above 300 ppm were shown to strongly promote the extent of UHC oxidation. Injection of hydrogen peroxide increased the degree of exhaust reactor oxidation and extended the oxidation further into the lean operation range.

A field engine was tested at increased NO_x levels, obtained by addition of ammonia to the air intake. No physical modifications of the engine or the settings were performed. The ammonia addition resulted in a reduction of unburned hydrocarbons by approximately 30% with CO_2 as the major product. Due to the comparatively low temperature and short residence time of the field engine exhaust system, as well as the absence of CO production, the UHC reduction was attributed to processes occurring in the cylinder or exhaust port, rather than in the exhaust system. Similar levels of UHC reduction prior to the exhaust reactor were observed in the test engine.

* E-mail: dgc@dgc.dk

† E-mail: chec@kt.dtu.dk

A detailed chemical kinetic model was used for simulation of the exhaust oxidation experiments. The modelling predictions were in fairly good agreement with the observations, confirming the catalytic role of NO_x in the oxidation of hydrocarbons. The model was used to extrapolate the test engine results to conditions representative of co-generation engines and the practical implications are discussed.

INTRODUCTION

In Denmark a significant share of the consumption of natural gas is used for co-generation of heat and power in lean-burn natural gas engines. The engines used are typically 1–4 MW_e with shaft efficiencies in the range 39–41% and thermal efficiencies from 85 to 95%. The capital costs of these units are comparatively low and they are suitable for de-centralised production of power and heat. A further advantage of this technology compared to conventional coal-fired power plants is the reduction of the CO_2 emission; the combustion of natural gas produces about 45% less CO_2 per energy unit compared to coal. However, the emission of unburned hydrocarbons (UHC) from these engines, which may amount to a significant fraction of the fuel input (Klimstra, 1990; de Wit *et al.*, 1998), has become a concern. Methane constitutes a large fraction of the UHC, and methane has a significant global warming potential. A number of studies on UHC emissions from spark ignition engines for natural gas (*e.g.* Klimstra, 1989; 1990; Thiagarajan *et al.*, 1994; Varde *et al.*, 1995) and for other fuels (*e.g.* LoRusso *et al.*, 1983; Cheng *et al.*, 1993; Huang *et al.*, 1996; Soudre *et al.*, 1997; Eng *et al.*, 1997a; 1998) have been reported and the hydrocarbon emission mechanisms are fairly well established. The major sources of UHC emissions from gasoline engines are crevices, non-vaporised fuel, oil layers, flame quenching and exhaust valve leakage (Cheng *et al.*, 1993). For natural gas fired engines the important sources of unburned hydrocarbons are filling of crevice volumes with unburned mixture that the flame cannot propagate into, flame quenching at the walls, and exhaust valve leakage. Since methane is more difficult to ignite than gasoline, misfiring of the engine may also be a significant source of UHC emissions (Johansson, 1995). Furthermore, for lean-burn gas engines, cycle-to-cycle variations due to unstable combustion may affect the UHC emission. Compared to gasoline engines, some sources of UHC are insignificant for gas engines: liquid fuel in the cylinder can be disregarded, methane solubility in oil is very low, and the cylinder deposits from natural gas combustion are reported to be minimal.

Control of unburned hydrocarbon emissions from lean-burn engines may be achieved by modifying the fuel, by modifying engine design and/or operating

conditions, or by applying post-cylinder processes such as catalytic oxidation or regenerative incineration. Another possibility is to enhance the post-cylinder oxidation process, either by modifying reaction conditions in the manifold/exhaust system or by injection of promoting additives.

Cheng *et al.* (1993) estimate that a significant amount of UHC is oxidised after the propagation of the flame, *i.e.* in the blow-down and exhaust process. However, it is known that ignition of methane is more demanding than ignition of other hydrocarbons. For autoignition after 1 ms (which is a realistic residence time in the early, hot exhaust channel), the necessary temperature for natural gas is about 1350 K, while it is only 950 K for gasoline (Bradley *et al.*, 1996). Cheng *et al.* (1993) report that two-thirds of the unburnt gasoline may be oxidised in the blow-down process and the exhaust channel; the post flame oxidation of methane and natural gas would be expected to be much lower. This difference in reactivity between methane/natural gas and other engine fuels has a significant effect on not only the amount, but also the composition of unburned hydrocarbons (Kaiser *et al.*, 1991; Cheng *et al.*, 1993; Drobot *et al.*, 1994; Raine *et al.*, 1997). The percentage contribution of unburned fuel to the hydrocarbon emissions vary from 95% for methane to 50% or below for gasoline and heavy hydrocarbons.

A significant oxidation of unburned hydrocarbons may take place in the exhaust port. Caton *et al.* (1983) estimate that depending on engine conditions as much as 70% of the hydrocarbons present may react. Drobot *et al.* (1994) report oxidation of various fuels, including methane, in the exhaust system of a single-cylinder engine. They find that, independent of fuel, a substantial reduction of UHC (about 40%) occurs in the exhaust port, but that reactivity in the downstream exhaust system is relatively minor. In general, gas phase chemistry in the manifold and exhaust channel has been considered to be small or negligible. However, this will depend on the exhaust system temperature. Laboratory experiments simulating engine exhaust conditions (Sorenson *et al.*, 1970; Sigworth *et al.*, 1970; Deller and Sorenson, 1986, Smith *et al.*, 1997) indicate that significant reaction, both hydrocarbon oxidation and NO to NO₂ conversion, may take place in the exhaust channel.

The objective of the present work was to evaluate the potential of exhaust oxidation of unburned hydrocarbons in lean-burn natural gas engines. The work involved experiments on a 35 kW test engine equipped with an extended exhaust reactor, field engine tests, and evaluation of the results through chemical kinetic modelling. The extent of exhaust oxidation of methane in lean-burn engines was assessed and the potential of enhancing the oxidation process by additive injection was evaluated.

EXPERIMENTAL

Natural gas test engine

The natural gas test engine was a Ford diesel engine converted for natural gas operation. It was a four-cylinder, four-litre displacement engine, operated slightly above 1500 RPM. A bowl had been machined in the piston crowns, lowering the compression ratio to 11:1. The gas engine was equipped with an Impco gas carburettor, a Garret type T2 turbocharger with waste-gate allowing for manual adjustments of charge pressure and a Mermaid type 4 water cooled inter-cooler. The engine was coupled to an asynchronous generator with a nominal load of 37 kW. The electricity generated was delivered to the main electricity supply net.

All measurements were performed at a fixed engine load of approximately 35 kW electric and both manifold and stack measurements were carried out at each setting. The exhaust reactor performance was established as function of engine stoichiometry and ignition timing. The O₂ in the exhaust was varied from 5% to above 9% (corresponding to excess air ratios λ of 1.28–1.75) and the ignition timing ranged from 24 to 18° before top centre.

Exhaust reactor

In order to evaluate the potential for oxidation of UHC in the exhaust channel the engine was equipped with an extended exhaust reactor. Thereby reaction conditions were better characterised and the high temperature residence time of the exhaust was increased from 40 ms to between 200 and 400 ms. The residence time was dependant on the engine stoichiometry since all experiments were performed at a constant load of 35 kW. The exhaust pressure was 1.6–1.8 bar during the experiments.

The engine was equipped with the original exhaust manifold, which collected the exhaust gases from the four cylinders. The manifold outlet led the gases through the specially designed and insulated exhaust reactor (Fig. 1). This reactor was made of stainless steel and consisted of an expansion cone (bendings and tubing of Ø 50 mm to Ø 129 mm) followed by a reactor tube. Finally, the gas was led through the contracting cone (Ø 129 mm to Ø 50 mm) to the turbocharger and afterwards to the stack. The total reactor volume was 0.0223 m³ and the surface area 0.73 m².

The exhaust reactor was designed within the practical limits to obtain the best possible turbulent plug flow conditions. Based on the methods described by Lev-

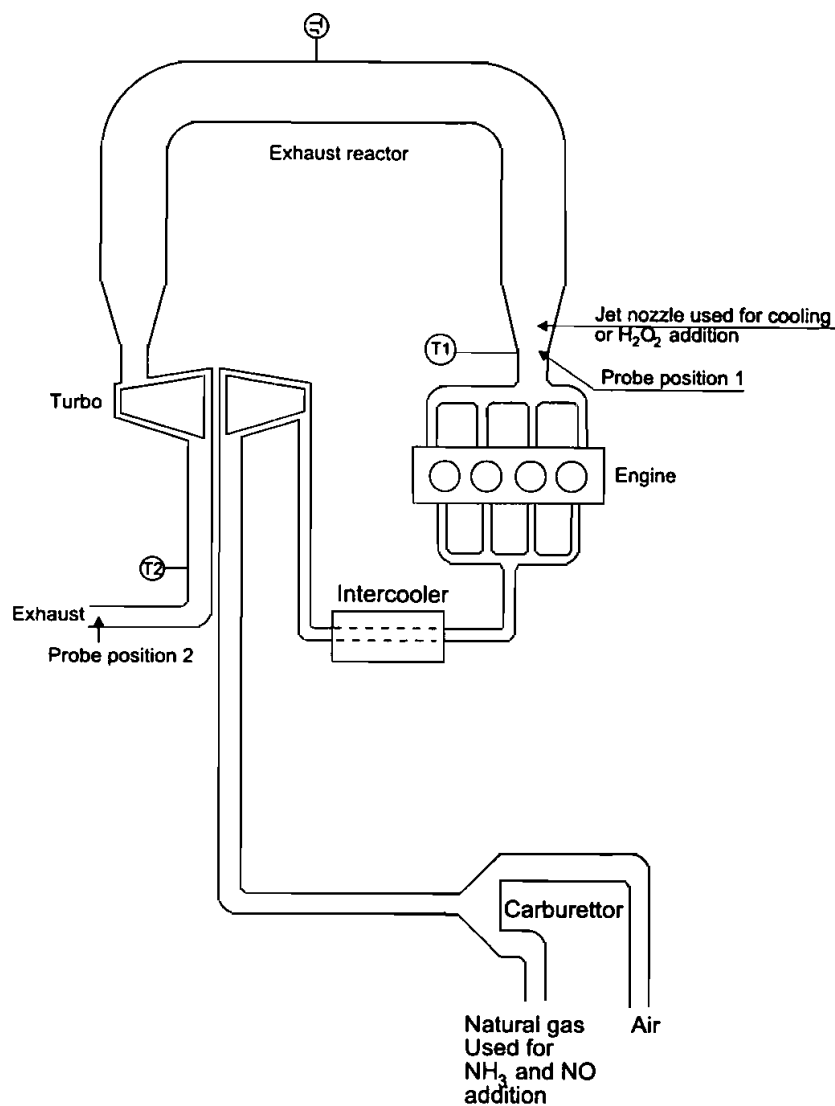


FIGURE 1 Gas engine and exhaust reactor

enspiel (1972) and Fogler (1986) we estimate that the reactor flow pattern in the exhaust reactor can be described as 10 to 40 perfectly stirred reactors in series. The average flow pattern in all the experiments will result in approximately 25 perfectly stirred reactors in series, *i.e.* a fairly good plug flow approximation.

At the reactor inlet fluctuations both in mass flow, composition and temperature had to be expected. According to Heywood (1988) the max/min ratio of the mass flows at the cylinder exhaust port during the exhaust process is approximately five. This number would be significantly lowered in the exhaust manifold where the exhaust of four cylinders was mixed, and at the reactor inlet position we estimate that the mass flow ratio was not larger than a factor of two. This fluctuation would quickly dissipate in the large volume reactor. Fluctuations in temperature and composition, though also significantly damped, are likely to affect the oxidation rate in the exhaust reactor, but their importance is difficult to assess. Normally temperature fluctuations would enhance fuel oxidation compared to isothermal conditions, but this effect may partly be offset, since higher temperatures to some extent may be linked with lower than average UHC levels.

Additive Injection and Temperature Control

During selected experiments the engine was operated with addition of NH_3 (or NO) in the natural gas intake or with H_2O_2 or air in the exhaust. The purpose of adding NH_3 was to increase the amount of NO_x in the exhaust, while hydrogen peroxide was used in an attempt to promote the exhaust oxidation process. Addition of air in the exhaust was done to control exhaust channel temperature independent of the engine settings and stoichiometry. The procedures are described in detail below.

The NO or NH_3 were added to the natural gas line from ordinary gas cylinders (see Fig. 1). Ammonia was the preferred additive for increasing the NO_x level, since gas cylinders with liquid NH_3 were available. Under conditions with high temperatures and high oxygen concentrations, NH_3 is largely oxidised to NO (Miller and Bowman, 1989). Such conditions prevail during the combustion process in the cylinders of the engine (Heywood, 1988) and a high conversion of the added NH_3 to NO would be expected. The NO or NH_3 may interact with the processes occurring in the cylinder. Nitrogen oxides may affect the auto-ignition chemistry (Eng *et al.*, 1997b), but little is known about the impact of NH_3 . However, experiments made in the present work on the test engine indicate that NH_3 and NO added in comparable quantities lead to a similar exhaust gas composition from the cylinder.

For injection of hydrogen peroxide into the exhaust gases, a dosage system was constructed. Evaporated hydrogen peroxide was led through a heated (150°C) stainless steel pipe into the exhaust manifold and injected in cross-stream. The decomposition rate of hydrogen peroxide is slow at temperatures below 150°C (Perry and Green, 1984). The experiments with hydrogen peroxide addition were all conducted with the ignition timing set to 24° .

The nozzle used for addition of hydrogen peroxide was also used to lower the temperature of the exhaust by addition of cooling air, up to 20% of the total mass flow. This way the exhaust channel temperature could be controlled independently of the cylinder process, but the oxygen concentration and dilution of the exhaust was changed.

Exhaust gas sampling and analysis

Exhaust gas sampling was performed in two positions, the manifold position and the stack position (Fig. 1). The manifold position was situated just before the reactor inlet, after the unification of the exhaust gas from the four cylinders, but prior to the nozzle for addition of hydrogen peroxide (or cooling air). The second exhaust gas sampling position was in the stack. This means that all results were based on a paired set of data, concentrations and temperature in the inlet of the reactor and in the stack.

Both exhaust gas sampling and temperature measurements at the reactor inlet position may be influenced by the non-steady flow and the non-homogeneity of the exhaust gas at the exhaust ports. However, since the sampling position was located after the unification of the exhaust gases and 40–50 cm from the exhaust ports, these fluctuations were expected to be of minor importance. Results reported by Hadjconstantinou *et al.* (1998) show that the fluctuation in composition decreases strongly as the sampling position is moved away from the exhaust port. The exhaust gas sampling procedure was further confirmed by the fact that at conditions where no reaction was expected only small deviations (<10% relative) were seen in the paired samples collected at the reactor inlet and in the stack.

A type K thermocouple logged the exhaust gas temperature. The exhaust gas samples were drawn through 6-mm outer diameter stainless steel probes, with an estimated cooling rate of 5×10^4 °C/s. This was sufficient to assure total quenching of the homogeneous CO oxidation chemistry at sample temperatures approaching 960°C (Flagan and Seinfeld, 1988). The sample gas flow rate exceeded 0.006 m³/min (0°C, 1 bar). The sample was led to the flue gas conditioner, where the gas was pumped, filtered, and dew point corrected to 0–2°C. Finally the gas was distributed to the gas analysers. Exhaust gas analysis was performed on conventional gas analysers for O₂, CO, CO₂ and NO/NO_x, while UHC was measured with a Flame Ionisation Detector (FID). The analysers were calibrated each day using test gases of ±2% relative uncertainty on the concentrations. Taking into account also the uncertainties on the instruments (linearity, temperature etc.), the expected accuracy of the analysis was 3–5%, dependent on component. The exhaust gas was not analysed for specific hydrocarbons, so the

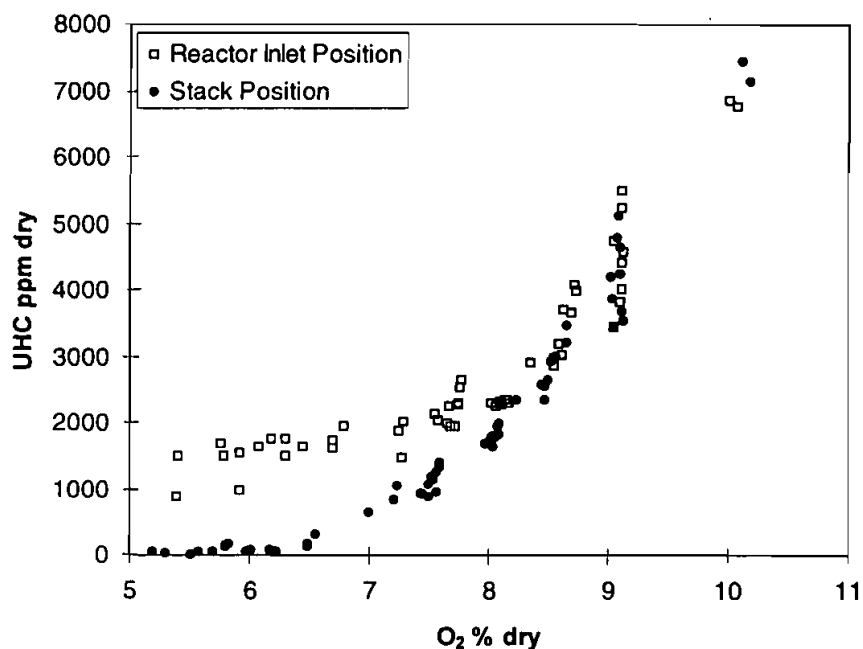


FIGURE 2 UHC content in the exhaust gas at the reactor inlet and stack measuring positions (basic operation experiments with ignition timing in the range 18–24° BTDC)

hydrocarbon speciation was not identified. However, previous work (Klimstra, 1989; 1990; Kaiser *et al.*, 1991; Drobot *et al.*, 1994; Raine *et al.*, 1997) indicate that for natural gas fired engines the UHC composition is similar to that of the fuel itself, in this case about 90% methane with smaller amounts of higher hydrocarbons.

Except where noted, all data points reported are average values of data collection periods of 500 seconds during stable engine operation with acquisition intervals of 2 seconds. All experimental data are reported on dry exhaust basis. For data with air dilution for cooling, corrections have been performed to coolant free basis.

TEST ENGINE RESULTS

The engine tests involved three specific types of experiments. The first type aimed at mapping the basic operating characteristics of the engine and the

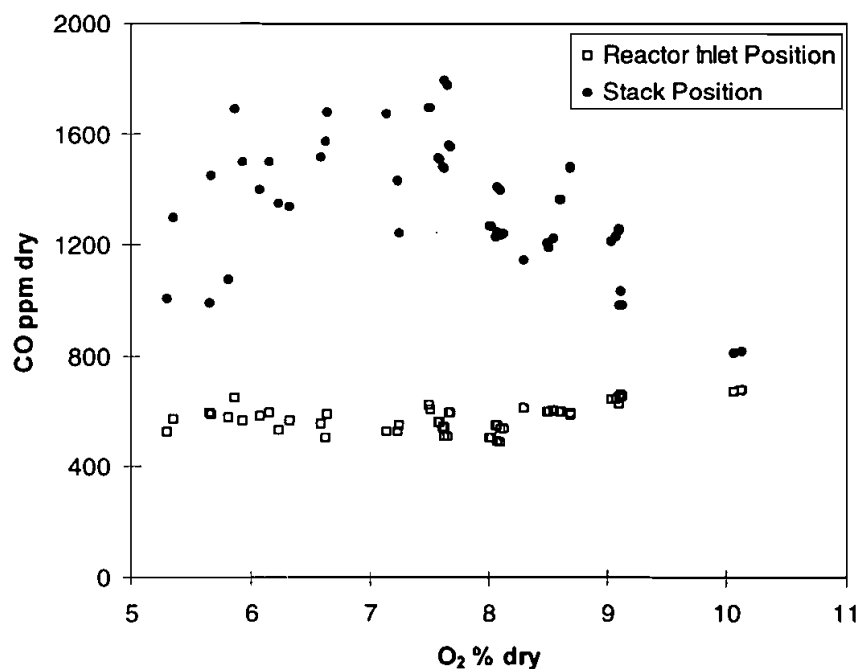


FIGURE 3 Measurements for CO in the stack and in the manifold (basic operation experiments with ignition timing in the range 18–24° BTDC)

exhaust reactor. The second type involved experiments, where only a single variable (*e.g.*, exhaust reactor temperature or NO_x level) was modified, while keeping the other variables essentially constant. Finally, in the third type of experiments, it was evaluated whether additives to the exhaust gas had an effect on the exhaust oxidation.

Basic Operation with Exhaust Reactor

The emission characteristics of the engine under basic operating conditions are outlined in Figs. 2–4. They show the concentrations of UHC, CO and NO_x in the exhaust gas at the manifold measuring position (*i.e.* at the exhaust reactor inlet). For UHC and CO also measurements from the stack position (*i.e.* after the exhaust reactor and turbocharger) are shown; for NO_x no significant difference was observed between concentrations at the two measurement positions.

The UHC measurements shown in Fig. 2 include all ignition timings tested; the observed scatter in data is due largely to differences this parameter. The amount

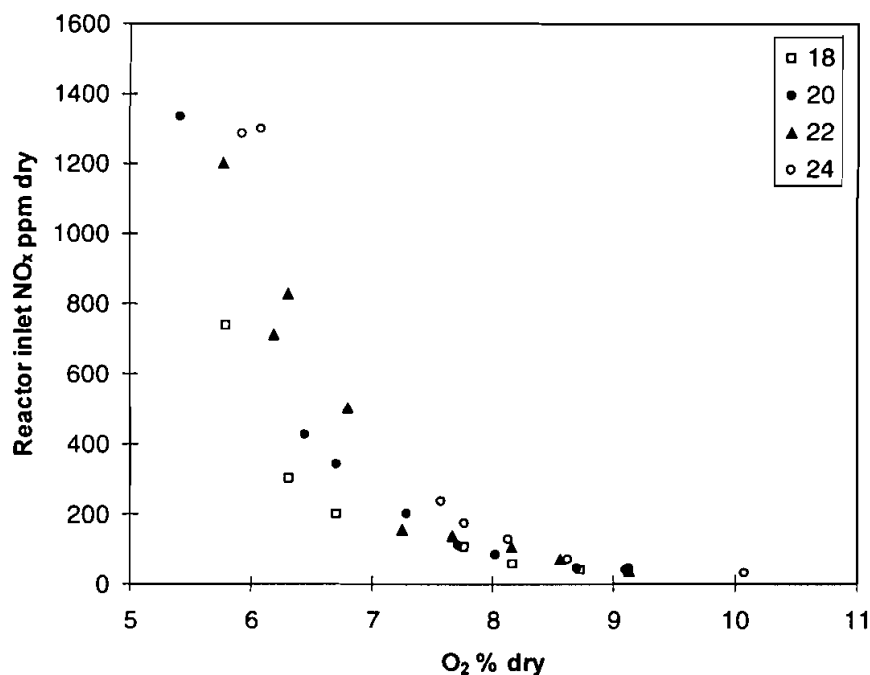


FIGURE 4 NO_x in reactor inlet position as function of exhaust oxygen and ignition timing (basic operation experiments)

of UHC is seen to increase sharply with an increase in oxygen level. The UHC level reaches a maximum of almost 7000 ppm at a stoichiometry corresponding to about 10% O₂ in the exhaust gas. Only a minor influence of crank angle was observed in the range investigated.

The mole fraction of CO in the manifold exhaust gas was almost constant at a level of about 550 ppm, independent of stoichiometry and crank angle (Fig. 3). Considering the large variation in UHC, the lack of change in CO concentration is surprising. The nitrogen oxides shown in Fig. 4 consist mostly of NO, consistent with the results of Klimstra and Westing (1995), but the partitioning among NO and NO₂ might be influenced by the sampling (Kramlich and Malte, 1978; Malte and Kramlich, 1980). As expected, the NO_x emission decreases strongly as the stoichiometry is leaned out. The NO is largely produced by the Thermal NO mechanism and correlates closely with the maximum temperature in the cylinder. This value decreases with increasing excess air (dilution). Also retarded ignition reduces the NO_x level due to a lowering of the peak temperature.

The presence of the exhaust reactor influences the UHC stack emission significantly (Fig. 2). As discussed above, the nominal exhaust reactor residence time

varied with stoichiometry during experiments, ranging from 200 to 400 ms. The exhaust temperature, measured as the reactor inlet temperature, was in average 675°C, ranging from 640 to 695°C dependant on ignition timing and stoichiometry. The average temperature drop from the exhaust manifold measuring position to the temperature logging after the turbocharger was 60°C. This decrease in temperature includes both the temperature drop caused by the gas expansion in the turbocharger and the heat released by oxidation of UHC.

In the exhaust reactor a large fraction of the UHC was oxidised at stoichiometries with less than 8% O₂. To allow comparison of the different experimental conditions, the data of Fig. 2 are shown in terms of UHC conversion in Fig. 5. The figure shows that the exhaust reactor at low oxygen concentrations is an efficient oxidation reactor for the UHC emitted from the manifold. However, as the stoichiometry is leaned out, the conversion efficiency of the exhaust reactor decreases significantly, approaching zero at O₂ levels above 9%.

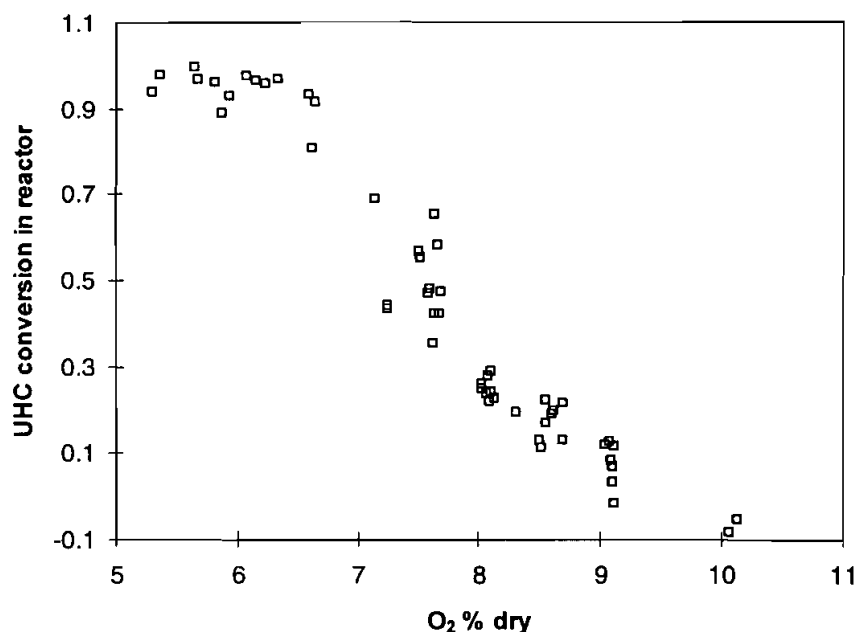


FIGURE 5 UHC reduction in the exhaust reactor as function of exhaust oxygen. Same data as shown in Fig. 2 (basic operation experiments)

The results of Fig. 3, in comparison with those of Fig. 2, show that the UHC oxidized in the exhaust reactor is mostly converted to CO, with a minor fraction oxidized to CO₂. The bell-shaped curve for CO at the stack position (Fig. 3) is

attributed partly to a somewhat higher efficiency at low oxygen levels (5–6%) in oxidizing UHC completely to CO_2 and partly to a lower amount of UHC oxidized in the exhaust reactor at high oxygen levels. In contrast to the findings for UHC and CO, very little change in nitrogen oxides concentrations over the exhaust reactor was observed.

In the basic operation tests discussed here, stoichiometry and ignition timing were the only controllable variables; all other parameters were dependant on these two variables. For such experiments that involve a complex interaction between variables, secondary effects may make it difficult to evaluate the experimental observations by pair-wise plotting of the variables. The strong correlation between the stoichiometry and the amount of UHC oxidized in the exhaust reactor (Figs. 2 and 5) must be attributed to second order effects. A change from 5 to 9% O_2 in the exhaust would not be expected to have a large inhibiting impact on the degree of reaction, provided other parameters were unchanged. Instead, the dependence of UHC on oxygen level might conceivably be attributed to the lower exhaust temperatures at lean conditions. Analysis of the engine data shows strong derived correlations between temperature, residence time and chemical composition. However, the results shown in Fig. 6 indicate that there is no simple correlation between the extent of UHC oxidation in the exhaust reactor and the reactor inlet temperature. Some of the scatter in the data are caused by uncertainties and fluctuations in the inlet and outlet values of UHC, in particular at lower UHC concentrations, but the spread in data above 650°C cannot be explained by these uncertainties. A somewhat better correlation (not shown) is obtained between UHC conversion and reactor residence time, but residence time effects can only partly explain the experimental observations.

Another parameter that might conceivably affect the UHC oxidation in the exhaust reactor is the concentration of nitrogen oxides in the exhaust gas. It is known that even small amounts of NO and/or NO_2 may interact strongly with fuel oxidation at low to medium temperatures (*e.g.* Norrish and Wallace, 1934; Bromly *et al.*, 1992; 1996; Amano and Dryer, 1998; Bendtsen *et al.*, 2000). Recently Eng *et al.* (1997b) showed that NO_x may also affect the autoignition chemistry in the cylinder of S.I. engines. In the present work a strong correlation, confirmed by principal component analysis (Bendtsen, 1999), between NO_x concentration and UHC conversion in the exhaust reactor was identified. This is illustrated in Fig. 7, which shows the UHC conversion as function of the inlet NO_x level for the basic operation test data, *i.e.* same conditions as in Figs. 2 to 6. In the range 50 to 300 ppm NO_x , the extent of UHC oxidation in the exhaust reactor increases dramatically with increasing nitrogen oxides concentration. At levels above 300 ppm NO_x full conversion of the UHC is observed. In order to verify the NO_x / UHC emission correlation, further tests were performed as discussed below.

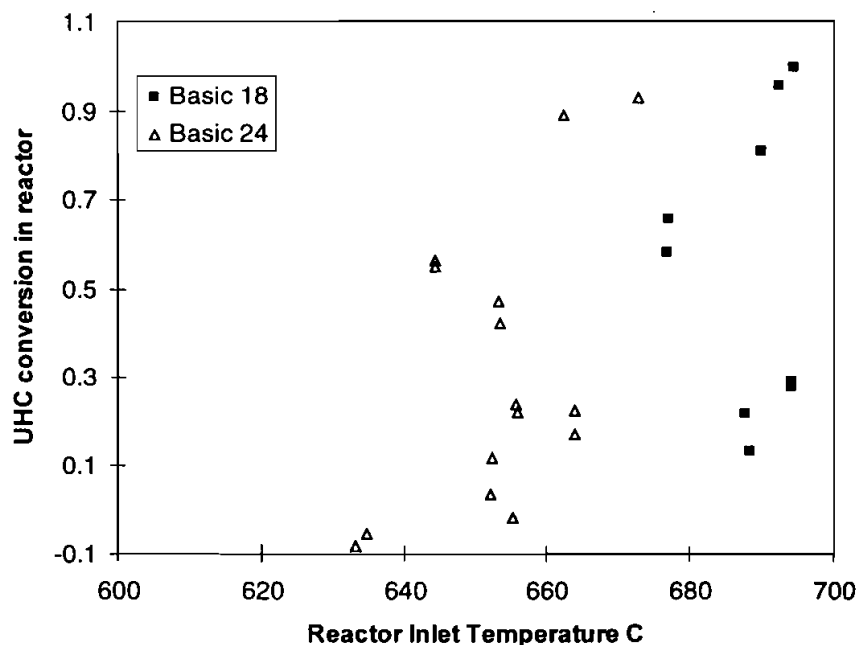


FIGURE 6 UHC conversion in the exhaust reactor as function of reactor inlet temperature for two different crank angles (basic operation experiments with excess air levels of 5–9% and ignition timing in the range 18–24° BTDC)

Effect of NO_x Level and Exhaust Temperature on UHC Emissions

In order to investigate further the correlation between UHC and NO_x levels, an additional series of experiments was carried out, in parallel with similar studies in a laboratory scale reactor (Bendtsen *et al.*, 2000). In the test engine experiments reported below the exhaust reactor temperature and NO_x concentrations were controlled independently of the engine settings by introducing ammonia and/or cooling air.

Introduction of NO or NH₃ to the gas intake (see Fig. 1) generally resulted in a decrease in UHC emission, both at the manifold probe position and in the stack. The reduction of UHC at the manifold, compared to no additive injection, was 15–35%. The mechanism of this reduction is not known at present. It was not possible to assess whether the decrease observed at this location in the engine exhaust was due to changes in the cylinder combustion process or to enhancement of oxidation occurring in the exhaust port. The reactive nitrogen components may interact with the processes occurring in the cylinder. Nitrogen oxides

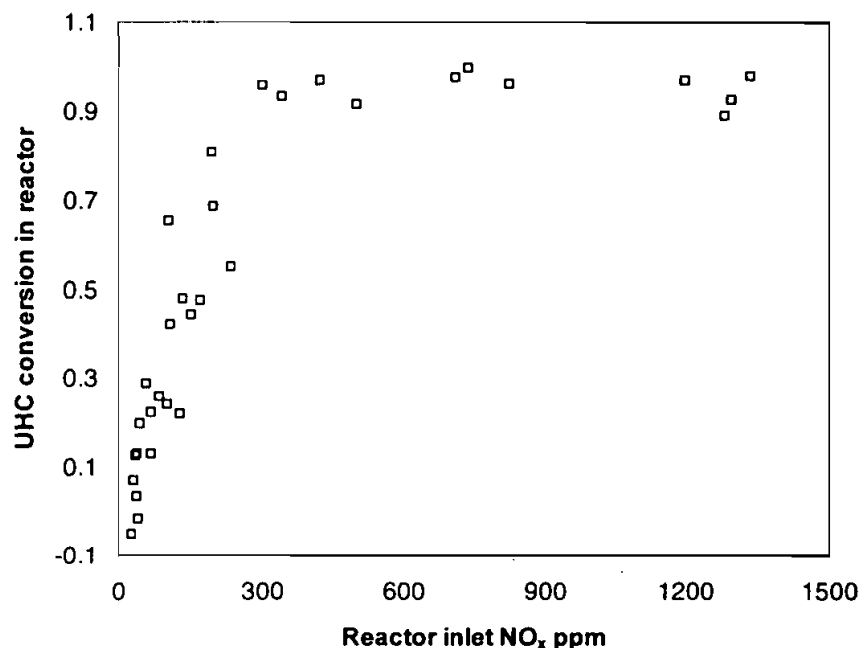


FIGURE 7 UHC conversion in the exhaust reactor as function of reactor inlet NO_x (basic operation experiments with excess air levels of 5–9% and ignition timing in the range 18–24° BTDC)

may affect the autoignition chemistry (Eng *et al.*, 1997b), but little is known about the impact of NH₃. However, for similar NO_x exhaust levels, no discernible difference in exhaust gas composition at the manifold position between NO and NH₃ addition was observed. It should be noted that since NH₃/NO are present in the inlet gas rather than in the burnt gas only, the effect on the cylinder chemistry may not be generally representative. Also, the effect of nitrogen oxides may be specific for lean-burn natural gas fired engines; Eng *et al.* (1997b) found no effect of NO addition on the in-cylinder UHC consumption for an S.I. engine run at close to stoichiometric conditions with n-butane as fuel.

Figures 8 and 9 show the dependence of the UHC conversion in the exhaust reactor on the reactor temperature and nitrogen oxides concentration. The results of Fig. 8 are obtained for one specific operating point of the engine. Without NO/NH₃ addition this specific engine setting resulted in NO_x levels of about 50 ppm and little UHC oxidation in the exhaust reactor. Controlling the temperature and NO_x as described above, the data clearly distinguish the effect of these parameters. It is seen that the UHC oxidation in the reactor correlates strongly with both temperature and nitrogen oxides concentration. Increase in any of these

parameters at temperatures above about 600°C yields a decrease in UHC emission; below 600°C little reduction of unburned hydrocarbons is observed.

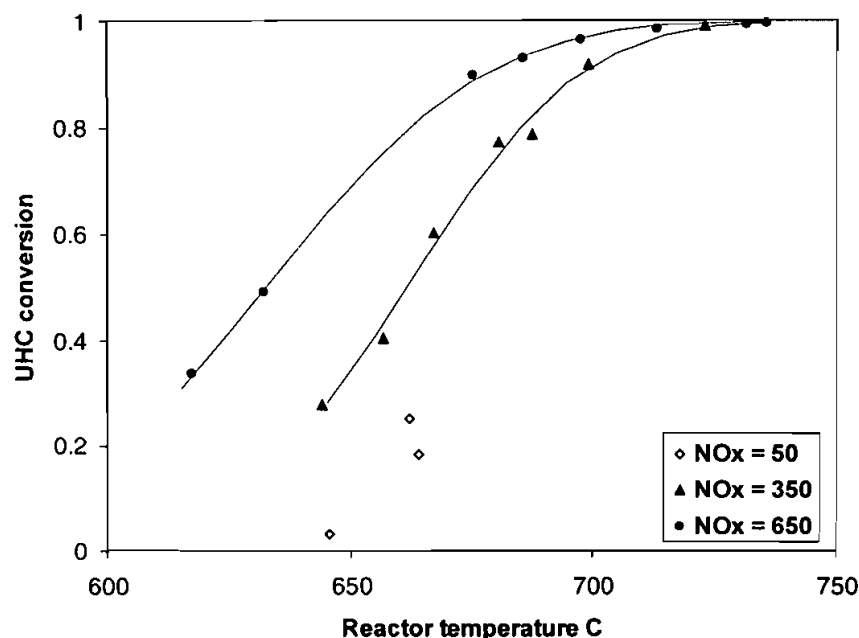


FIGURE 8 The exhaust reactor conversion of UHC as function of the reactor temperature. The engine settings (stoichiometry and ignition timing) are held constant, while reactor temperature and NO_x exhaust level are varied by means of additives and cooling. The cylinder stoichiometry corresponded to an oxygen level of about 9%

The results shown in Fig. 9 are obtained at three different stoichiometries, but with a fixed NO_x exhaust level of 650 ppm. The conversion was calculated with respect to the actual dilution used during the experiments. The data confirm the results of Fig. 8, that at fixed levels of nitrogen oxides a strong correlation is obtained between exhaust reactor temperature and UHC conversion. The influence of the stoichiometry is seen to be small, and the scatter in Fig. 9 may as well be caused by differences in inlet concentration and available residence time.

The results confirm that increased NO_x levels do improve the UHC conversion in the exhaust reactor, provided temperature and reaction time is sufficient. The fact that the nitrogen oxides concentrations do not change significantly in the exhaust reactor, despite a high level of UHC conversion, shows that the promoting effect of NO_x is catalytic in nature. The process is found to be insensitive to the engine stoichiometry, but very dependent on the NO_x level and the exhaust

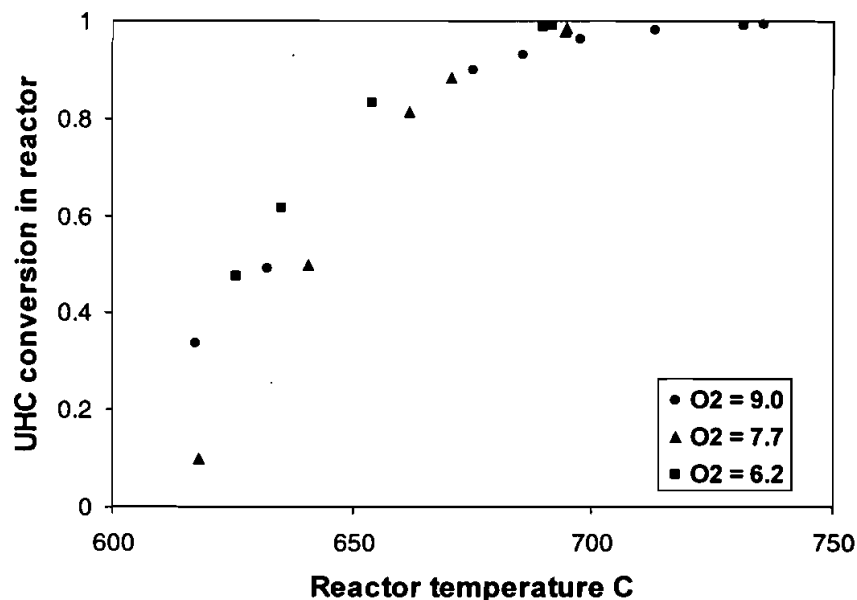


FIGURE 9 The exhaust reactor conversion of UHC as function of the reactor temperature for different engine stoichiometries. For each stoichiometry the engine settings were held constant, while reactor temperature were varied by means of cooling. The NO_x exhaust level was 650 ppm dry in all tests (regulated by additive injection)

reactor temperature. The mechanism for the NO_x sensitised UHC oxidation in the exhaust reactor is discussed below.

Hydrogen peroxide addition

In order to promote the oxidation chemistry of the exhaust reactor, addition of hydrogen peroxide to the exhaust reactor was performed. By decomposing into reactive species, mainly OH radicals, the hydrogen peroxide initiates a chain of reactions that may enhance the oxidation of the UHC. Figure 10 shows the effect of hydrogen peroxide addition on the UHC emission. The experimental tests were performed with two different quantities of injected hydrogen peroxide solution, corresponding to levels of 30–40 ppm and 130–150 ppm, respectively, in the exhaust gas.

The injection of hydrogen peroxide caused a considerable reduction in the stack emission of UHC. The hydrogen peroxide is seen to activate the oxidation chemistry at lean conditions, where in the absence of this additive, no or very lit-

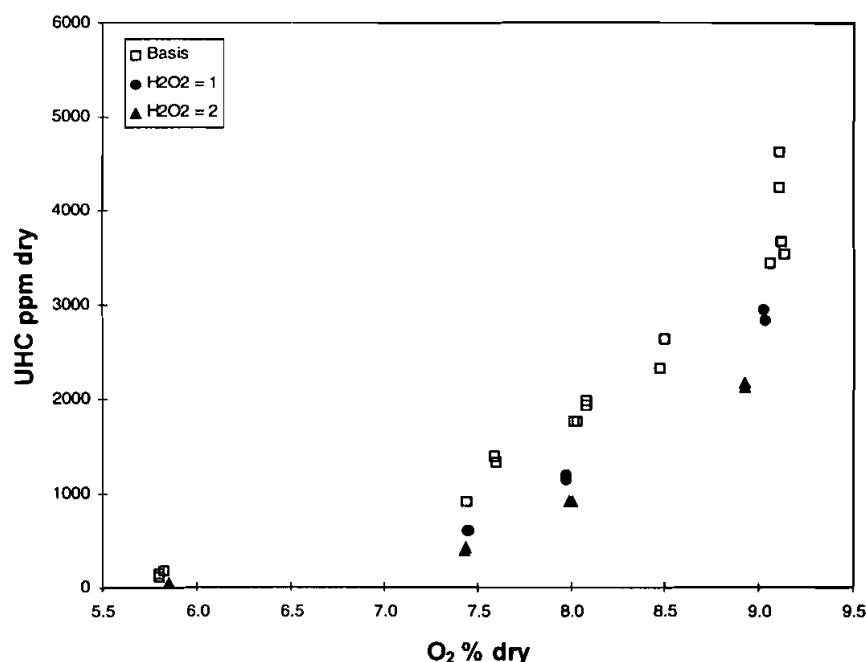


FIGURE 10 Emission of UHC with and without injection of hydrogen peroxide in the exhaust reactor as function of stoichiometry. The hydrogen peroxide was injected as a 35%w/w solution. "H₂O₂ = 1" denotes a H₂O₂ level in the reactor inlet of 30–40 ppm, while "H₂O₂ = 2" corresponds to a reactor inlet level of 130–150 ppm. The ignition timing was 24° BTDC

the UHC oxidation was seen in the exhaust reactor (Fig. 2). The NO_x emission was not affected by the addition of hydrogen peroxide. However, the CO emission from the reactor changed. At O₂ levels below 8%, the addition of hydrogen peroxide promoted both UHC and CO oxidation and caused the CO emission to decrease slightly. At higher O₂ levels, the increased amount of UHC oxidized is converted almost quantitatively to CO.

The fact that an increased amount of hydrogen peroxide results in an increased oxidation in the reactor (Fig. 10) shows that the oxidation chemistry is not self-sustaining under these conditions. Since both the H₂O₂/UHC ratio and the temperature decrease as the O₂ level is increased, a lower efficiency of the additive injection would be expected at leaner conditions. This is confirmed by the observations; the stack emission of UHC is reduced by about 60% at 6–7% O₂, but only up to 40% at 9% O₂. Model extrapolations of the test engine results to practical conditions with lower temperatures and shorter residence times are discussed below.

MODELLING

In order to analyse the interaction between UHC and NO_x emissions and to develop a predictive tool for the exhaust oxidation process, the engine results were interpreted in terms of a detailed chemical kinetic model. The model was used to extrapolate test results to the conditions of full-scale co-generation gas engines.

Numerical Procedure

In the modelling, we have assumed that the exhaust system from the engine manifold to the stack can be described as an isothermal plug-flow reactor. Furthermore it was assumed that the chemical processes freeze when the gas passes the turbo charger. The modelling was conducted with a plug flow code in connection with a detailed reaction mechanism describing methane oxidation. We used the SENKIN program (Lutz *et al.*, 1989), which is part of the CHEMKIN-II package (Kee *et al.*, 1989). For the simulations, we apply the chemical kinetic model of Bendtsen *et al.* (1999), which was developed based on flow reactor studies of CH_4 oxidation under conditions similar to engine exhaust. The reaction set involves 77 species and 484 elementary reactions.

Exhaust Reactor Chemistry

In the modelling we have assumed the hydrocarbon partitioning at the inlet to the exhaust reactor to be the same as in the fuel. This assumption is supported by a number of studies on natural gas engines that show the UHC composition to be largely the same as that of the gaseous fuel (Klimstra, 1989; 1990; Kaiser *et al.*, 1991; Drobot *et al.*, 1994; Raine *et al.*, 1997). Pooling the higher hydrocarbons as ethane, we have assumed the UHC to consist of 90% methane and 10% ethane. The effect of the uncertainty in the exhaust reactor inlet composition is discussed below.

Figure 11 shows comparison between test engine data and modelling predictions for UHC and CO as function of the NO_x concentration in the exhaust gas. These data were obtained as part of a preliminary screening study; no concentration measurements at the exhaust reactor inlet are available and results are shown for oxygen levels of both 8% and 9%. Furthermore, some of the observed UHC oxidation caused by the higher NO_x level may be attributed to processes in the cylinder or manifold. For these reasons, conditions in the exhaust reactor are less well-defined than for the other data shown in the present paper. However, the

data show clearly the correlation between UHC, CO and NO_x at typical reaction conditions in the exhaust reactor. As the NO_x level increases from about 50 ppm to 300 ppm, the UHC emission decreases from about 4000 ppm to very low levels, while the CO level increases strongly. The CO reaches a maximum at 200–300 ppm NO_x . Above 500 ppm NO_x , the UHC is completely oxidized, while the emission of CO shows a minimum between 500 and 1000 ppm NO_x . At high levels of nitrogen oxides, above 1000 ppm, both UHC and CO emissions increase slowly with increasing amounts of NO_x . The data are in qualitative agreement with laboratory findings (Glarborg *et al.*, 1995), showing that small amounts of NO enhance CO oxidation, while higher concentrations of NO tend to inhibit CO oxidation due to removal of radicals.

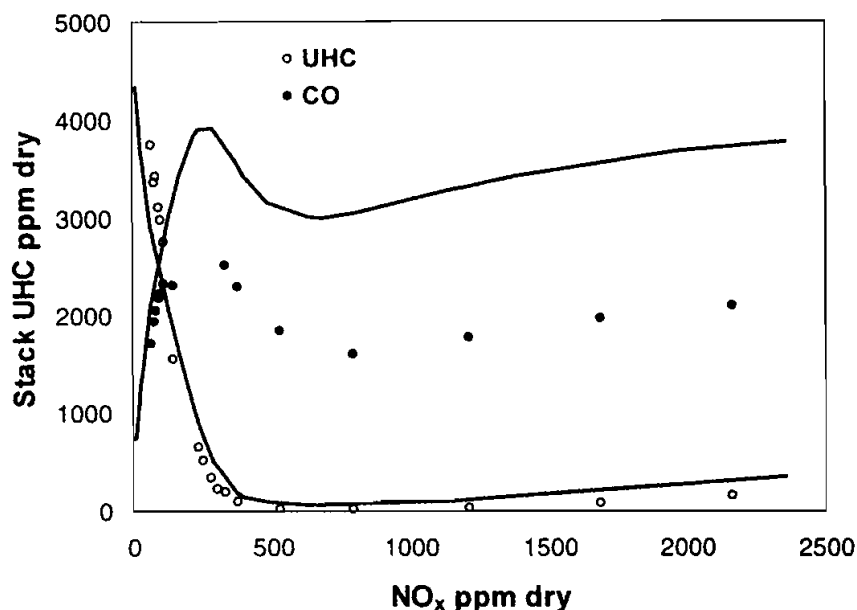


FIGURE 11 Comparison between measured and predicted stack concentrations of UHC and CO as function of NO_x in the exhaust. Note that in these experiments NO_x was increased by adding NO to the natural gas. Data were collected over periods of approximately 200 seconds. Due to analyser saturation, CO concentrations above 2540 ppm occurring at levels of NO_x of 200–300 ppm are not shown. Data are shown for excess air levels of 8% (above 200 ppm NO_x) and 9% (0–300 ppm NO_x). Modelling assumptions: inlet composition $\text{CH}_4 = 4410$ ppm, $\text{C}_2\text{H}_6 = 490$ ppm, $\text{O}_2 = 8.5\%$, $\text{H}_2\text{O} = 13\%$, $\text{CO}_2 = 6.5\%$, $\text{NO} = 10\text{--}1813$ ppm, $\text{NO}_2 = 3\text{--}544$ ppm, balance nitrogen; temperature = 680°C , reactor residence time = 210 ms, pressure = 1.7 bar

The complex behaviour shown in Fig. 11 is described well by the kinetic model. The model predicts correctly the strongly promoting effect of NO_x , even

in lower concentrations, on UHC oxidation; the behaviour of CO with the early peak, resulting from partial oxidation of UHC, and the minimum occurring at slightly higher NO_x levels; and also the slight inhibition observed at high concentrations of nitrogen oxides. The difference observed in the CO level can largely be attributed to over-estimation of the UHC reactor inlet concentration for higher NO_x levels. For simplicity the calculations were performed with a constant reactor inlet composition (except for NO_x). However, at 300 ppm NO_x the data shift from being mostly 8% O_2 data (high UHC) to being solely 9% O_2 (lower UHC). Furthermore, in-cylinder UHC reduction caused by increased NO_x levels has been neglected.

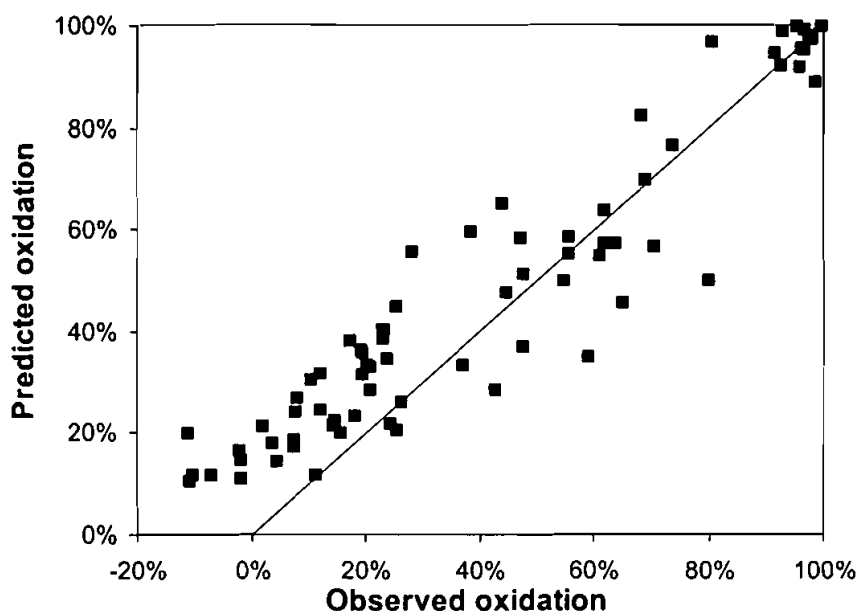


FIGURE 12 The observed versus predicted extent of UHC oxidation in the exhaust reactor. The line corresponds to a perfect match between model and experiments

Figures 12 and 13 show the correlation between measured and predicted UHC and CO, respectively. The figures include all the available data from the test engine experiments, except those of Fig. 11. These data are obtained under reaction conditions that are more accurately known than those of Fig. 11. The model predicts the oxidation of THC satisfactorily (Fig. 12), but with a tendency to over-predict the extent of oxidation. The qualitative prediction of the correlation

between NO and oxidation of THC is good, and the deviations between the model and observations correspond to the steep part of the UHC conversion curve shown in Figure 7. The stack levels of CO were also predicted fairly well by the kinetic model (Fig. 13). However, for some conditions the CO concentration is under-predicted, mainly because the model tend to overestimate the degree of oxidation of CO to CO₂ at lower temperatures.

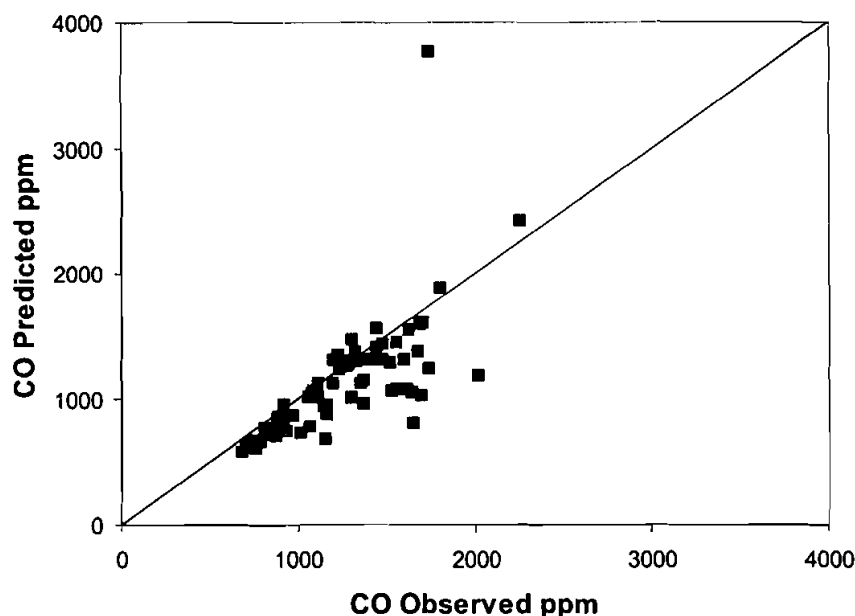


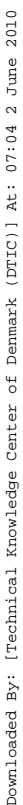
FIGURE 13 The observed versus predicted concentration of CO (moist) in the stack. The line corresponds to a perfect match between model and experiments

The influence of uncertainties in the experimental conditions on model predictions was analysed. The dominant source of error is likely to be variation in temperature. A change in reactor temperature as small as 20°C may cause a significant change predicted UHC, while a change in pressure of ± 0.3 atm, has only a minor impact on modelling predictions. A particular concern was the uncertainty in the exhaust gas composition at the reactor inlet, *i.e.* partitioning of unburned hydrocarbons, presence of partially oxidised species like formaldehyde, radical level, and NO/NO₂ ratio. A systematic study of the effect of changes in these parameters within their uncertainty showed, however, that they had only a minor impact on modelling predictions. It is noteworthy that even a

change of UHC composition from simulated natural gas (90% methane and 10% ethane) to pure methane causes only a modest decrease in reactivity, in apparent contrast to shock tube ignition delay experiments reported in literature (*e.g.* Spadaccini and Colket, 1994). The reason is that under the conditions investigated in the present study the enhancing effect of higher hydrocarbons and partially oxidised species on methane oxidation is minor compared to the promotion caused by the presence of nitrogen oxides.

Figure 14 shows the mechanism for UHC oxidation promoted by nitrogen oxides (Bendtsen *et al.*, 2000). The oxidation of methane proceeds through the methyl radical, CH_3 , which is comparatively un-reactive. For this reason, the fate of CH_3 has a large impact on the overall fuel oxidation rate. At elevated temperatures or in the absence of NO_x , CH_3 reacts with O_2 to form CH_2O (path A). Formaldehyde is further oxidised through a sequence of reactions to CO and finally CO_2 . In the presence of NO_2 , however, CH_3 reacts instead with NO_2 to form CH_3O , which rapidly decomposes thermally to CH_2O and a H atom (path B). Due to the activation energy of the reactions, at temperatures around 600–800°C path B from CH_3 to CH_2O is faster than the one step path (A) dominating at higher temperatures. Furthermore, due to the H atom formed in path B, this path is overall chain branching, in contrast to path A. The consumed NO_2 in path B is largely regenerated, *i.e.* the process can be regarded as a catalytic reaction. If NO is present without NO_2 , a three step path involving formation of CH_3O_2 , CH_3O and CH_2O becomes active instead (path C). However, path C also produces NO_2 , and as soon as a few ppm NO_2 is formed, path B becomes dominant. Since nitrogen dioxide is always present in the exhaust from lean burn gas engines (Klimstra and Westing, 1995), path C is of minor importance.

Since the model provides a fairly good description of the chemical processes occurring in the exhaust, it can be used to extrapolate the engine test results to practical conditions. The manifold temperature of full-scale co-generation engines is in the range 450–650°C, depending on cylinder conditions and whether the exhaust system is cooled. Figure 15 shows model predictions for a practical engine, using a representative exhaust gas composition, exhaust residence time and pressure. It is seen that even in the range from 550 to 650 °C, *i.e.* the upper part of the exhaust temperature range of these engines, less than 20% oxidation of UHC occurs in the exhaust system. This indicates that for the typical co-generation engines only little oxidation of UHC will occur in the exhaust system. Both test engine results and modelling show that even at high NO_x levels, temperatures above 600 °C is required. Even though, in general, newer engines are designed with higher exhaust temperatures, reaction conditions in the exhaust would have to be altered to obtain a significant oxidation of UHC in this part of the engine.



The UHC, which is converted in the exhaust system, is only partly oxidised. The major product of oxidation is CO, but also aldehydes, primarily formaldehyde, may be emitted. The modelling predictions of Fig. 15 indicate that signifi-

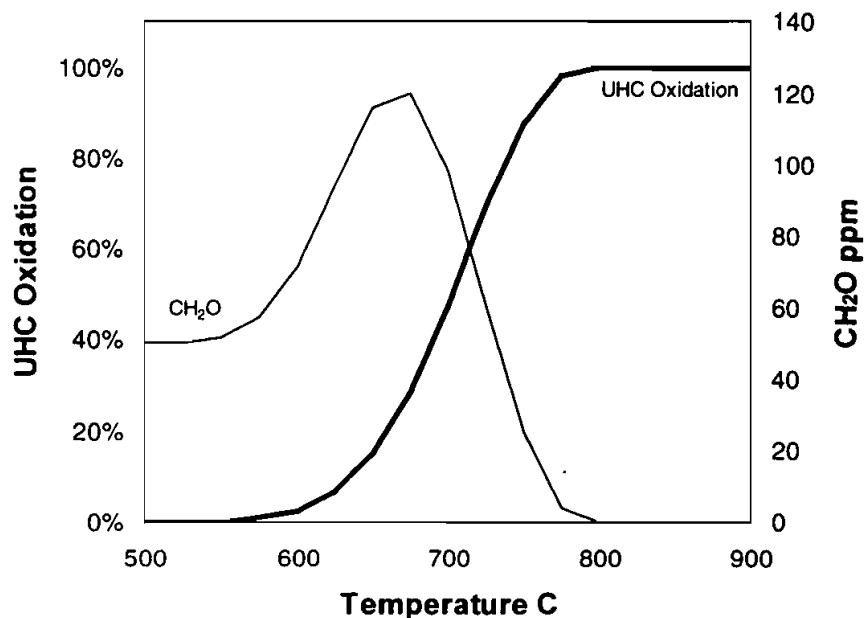


FIGURE 15 A simulation of the exhaust oxidation under co-generation engine conditions with varying temperature. The calculations show UHC oxidation and CH_2O concentration. Inlet composition: 2600 ppm CH_4 , 160 ppm C_2H_6 , 50 ppm CH_2O , 210 ppm NO , 50 ppm NO_2 , 7.8% O_2 , 11.5% H_2O , and 6.1% CO_2 , balance nitrogen. Residence time is 50 ms and pressure is 1.7 bar

cant amounts of formaldehyde may be formed in the exhaust system at conditions, which result in only minor conversion of UHC. Emission of aldehydes from natural gas engines has become a concern, in particular due to their adverse impact on the near environment. In the present study no measurements of CH_2O were performed. However, we have used laboratory data reported by Bendtsen *et al.* (2000) in combination with detailed kinetic modelling to assess whether a simple correlation between emissions of CH_2O and CO could be identified. The laboratory data were obtained under conditions similar to those of the engine exhaust system, except for a lower pressure. Figure 16 shows that temperatures exist for which high concentrations of either CO, CH_2O or both may be found. Carbon monoxide is a significant product of 20–90% partial oxidation of methane, while CH_2O is mainly produced with less than 50% oxidation. Accordingly, a typical field study of these two parameters under varying conditions cannot be expected to reveal a correlation between CO and CH_2O and it may be difficult to identify simple correlations between CH_2O emissions and other emissions; also for full-scale engines.

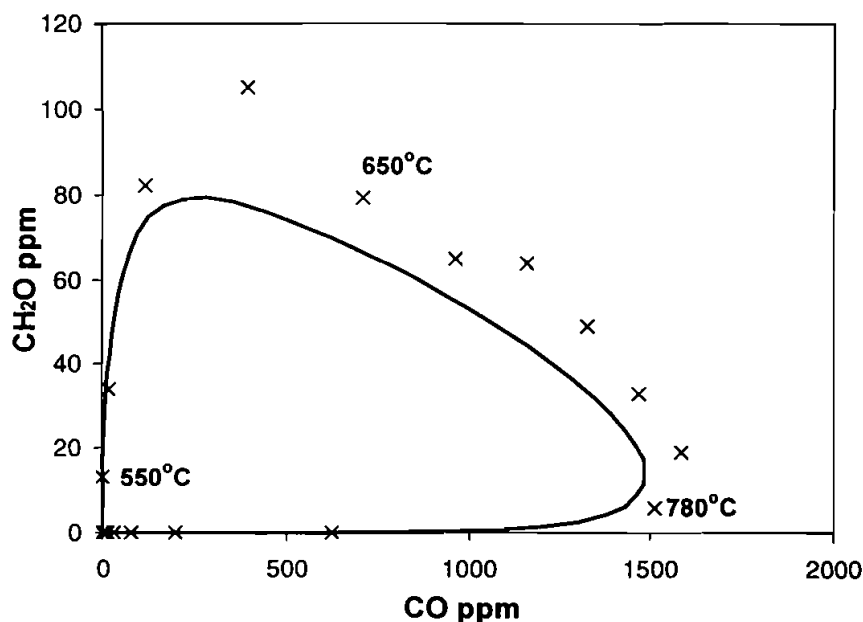


FIGURE 16 Correlation between CO and CH₂O emissions from flow reactor oxidation of methane. Symbols denote laboratory measurements (Bendtsen et al., 2000), lines denote modelling. Conditions are 2240 ppm CH₄, 210 ppm NO, 3.9% H₂O and 3.6% O₂. Temperatures range from 500 to 1000°C. Residence time was 193–318 ms dependent on temperature (calculated in seconds as $246/T$ with temperature in K)

Hydrogen peroxide addition

The model was also used to investigate the mechanism of the effect of H₂O₂ addition and to extrapolate the results to conditions more representative of practical engines. Model predictions compared well with the H₂O₂ addition data shown in Fig. 10, indicating that the model could be used for extrapolation with some confidence.

In order to assess the combined effects of the levels of hydrogen peroxide and NO/NO₂ present in the flue gas and to identify the optimal conditions for addition of hydrogen peroxide to the exhaust manifold, a series of simulations with the detailed chemical kinetics flow reactor model was made. Figure 17 shows the predicted effect of H₂O₂ concentration, temperature and reaction time on the UHC emission. The temperatures covered correspond to the upper part of the range encountered for co-generation engines, as discussed above.

Model predictions indicate that the effect of hydrogen peroxide is not very sensitive to the NO/NO₂ ratio in the exhaust gas, but that a certain amount of nitro-

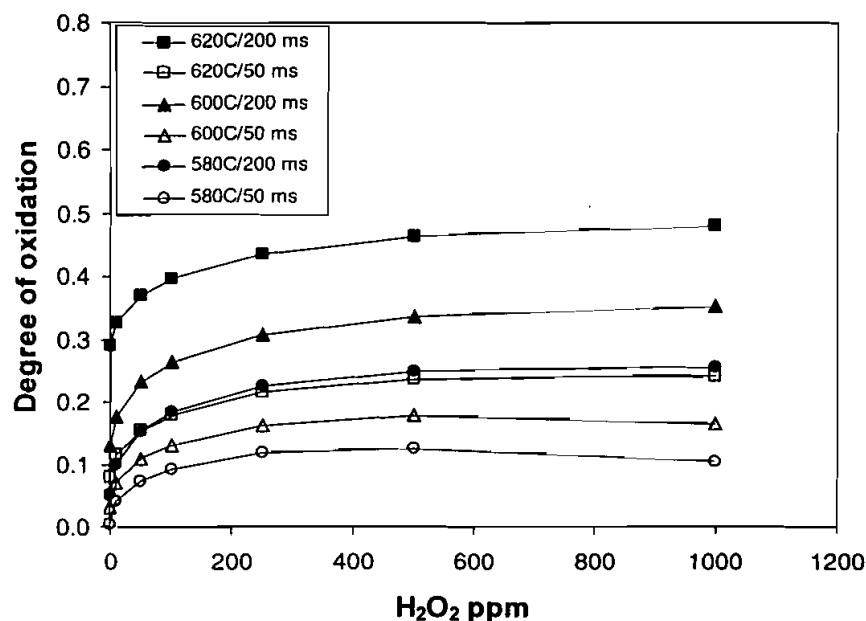


FIGURE 17 The effect of hydrogen peroxide concentration on the oxidation of methane. Solid curves correspond to a residence time of 200 ms and dashed curves to 50 ms. Calculations are made for temperatures of 580°C, 600°C, and 620°C. Inlet conditions: 3500 ppm CH₄, 250 ppm NO and 50 ppm NO₂

gen oxides enhances the UHC oxidation. An increase in H₂O₂ results in an increase in the extent of methane oxidation. However, the effect of adding extra H₂O₂ is dependent on temperature and residence time. In general the benefit of increasing the concentration of H₂O₂ beyond 250 ppm is comparatively small under the conditions investigated.

FIELD TEST RESULTS

As a consequence of the significant UHC reduction obtained in the test engine with the exhaust reactor, field tests at increased NO_x levels were performed at a co-generation plant installed in Denmark. The gas engine was a Caterpillar 3516 SI V16 lean burn open chamber gas engine with a rated shaft power of 1070 kW and an engine speed of 1500 rpm. The engine had accumulated 30.000 h of operation.

The engine had an air intake system with two air filters and two turbochargers. The natural gas was added to the air prior to the turbochargers. The gas/air mix-

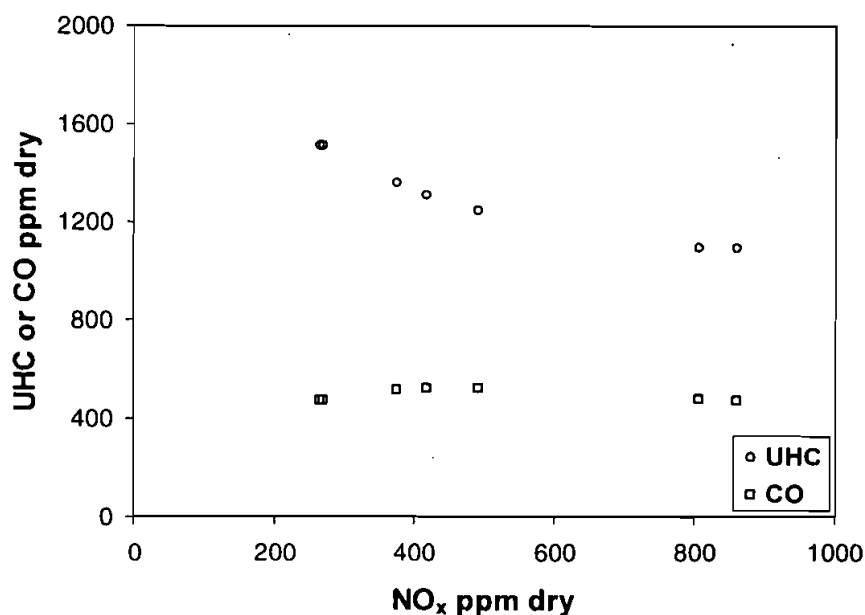
ture was led to a single inter-cooler. Similarly to the test engine experiments, ammonia was added upstream of the cylinder to increase the NO_x level. This was done by adding NH_3 in order to obtain levels of NO_x similar to those of the test engine experiments. In order to obtain the best possible distribution, the NH_3 was added to both air intakes. A pressure-balanced system was used to ensure almost equal dosage to both air intakes. The NH_3 /air/gas mixture passed through the turbochargers and the inter-cooler, resulting in a fairly uniform mixture. The amount of NH_3 added was not measured during the full-scale tests. Engine damage was not observed due to the addition of NH_3 , nor did the lubrication oil analysis performed in the field test show any differences compared to normal analysis data.

Figure 18 shows the results of the full scale test. The UHC emission on the full-scale engine is seen to correlate with the exhaust NO_x level; UHC decreases monotonically as NO_x increases from 250 ppm to above 800 ppm. The highest UHC reduction, obtained at the NO_x levels of 800–900 ppm, was 28%, a reduction from 1500 ppm to below 1100 ppm. This reduction most likely takes place in the cylinder or exhaust port. The average temperature at the exhaust ports was 540–570 °C and the residence at this temperature comparatively short, *i.e.* conditions that are unfavourable for significant reaction in the exhaust channel. The lack of oxidation in the exhaust system is confirmed by the fact that no significant increase in CO emission is detected.

If the lower temperature is taken into consideration, the field engine results correspond qualitatively to the observations from test engine experiments. However, the mechanism for the reduction in UHC emission remains to be identified. As for the test engine, it was not possible to assess whether the reduction in UHC emission was due to changes in the cylinder combustion process or to enhancement of oxidation occurring in the exhaust port. Furthermore, it is not known presently, whether the effect was caused directly by the added ammonia or by the increased NO_x level resulting from NH_3 oxidation. Additional work is required to resolve these issues.

CONCLUSIONS

Exhaust manifold oxidation of unburned hydrocarbons was studied using a 35 kW test engine operating under lean-burn conditions with natural gas. The engine was equipped with an exhaust reactor to extend the residence time. Results indicate that under proper reaction conditions a significant oxidation of unburned hydrocarbons may take place downstream of the cylinder. The oxida-

FIGURE 18 Full-scale test results of NH_3 addition to a co-generation engine

tion of UHC in the exhaust reactor strongly correlates with the concentration of nitrogen oxides in the exhaust, since NO_x has a catalytic effect on the oxidation process at low temperatures. The manifold oxidation process involves partial oxidation of the UHC and may lead to enhanced emissions of CO and aldehydes. Injection of hydrogen peroxide both increased the degree of exhaust reactor oxidation and extended the oxidation further into the lean operation range.

Operation at increased NO_x levels was tested on a field engine without any physical modifications. The emission of unburned hydrocarbons was reduced by approximately 30%. Due to the low temperatures and short residence times in the exhaust system, the enhanced UHC oxidation is attributed to processes occurring in the cylinder or exhaust port. Similar levels of UHC reduction prior to the exhaust reactor were observed in the test engine.

The experimental results from the exhaust reactor of the test engine were analysed by simulations using a detailed chemical kinetic model. The mechanism for the observed catalytic effect of NO_x on the oxidation of unburned hydrocarbons was identified. In addition the model was used to extrapolate the test engine results to conditions of interest for co-generation gas engines, in order to assess the practical implications.

Acknowledgements

The authors wish to acknowledge the financial support of the Danish gas companies, The Danish Department of Energy (grant no. EFP-1323/96), the CHEC Research Centre and Gaz de France. NESA is acknowledged for making the co-generation engine available for the field tests. The authors wish to thank Professor Fred Dryer and Dr. Jacob Klimstra for helpful comments.

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