Environmental optimisation of natural gas fired engines

Measurement on four different engines

Project report
October 2010

RAPPORT

Dansk Gasteknisk Center a/s • Dr. Neergaards Vej 5B • 2970 Hørsholm • Tlf. 2016 9600 • Fax 4516 1199 • www.dgc.dk • dgc@dgc.dk

Environmental optimisation of natural gas fired engines

Measurement on four different engines

Torben Kvist

Danish Gas Technology Centre
Hørsholm 2010

Title	:	Environmental optimisation of natural gas fired engines
Report Category	:	Project report
Author	:	Torben Kvist
Date of issue	:	June 2010
Copyright	:	Dansk Gasteknisk Center a/s
File Number	:	732-46; H:\732\46 Miljøoptimering af gasmotorer\Rapportering\Samlet endelig rapportering\10089 measurements.doc
Project Name	:	Environmental optimisation of natural gas fired engines
ISBN	:	978-87-7795-329-3

Table of Contents Page

1 Introduction

Emissions of unburned hydrocarbons (UHC), NO_x and CO from stationary natural gas fired engines are regulated according to "Bekendtgørelse nr. 621 of 23/06/2005". The threshold values of these emissions for stationary natural gas fired engines are:

NO_x: 550 mg/m^3(n) @ 5 % O_2
UHC: 1500 mg/m^3(n) @ 5 % O_2 and 30 % electrical efficiency
CO: 500 mg/m^3(n) @ 5 % O_2

Today there is no threshold value for formaldehyde (HCHO). However, the Danish Environmental Protection Agency suggests 22 mg/m^3(n) @ 5 % O_2 and 30 % electrical efficiency. This suggestion was submitted for hearing in December 2008 and it is expected that it will be valid later 2010.

The threshold value of unburned hydrocarbons is given as the concentration of C atoms in the hydrocarbons compounds. That means that all hydrocarbons are weighted equally (relative to number of C atoms) despite difference in harmfulness.

Emissions can be reduced by both improved engine design and by modifying the engine settings. Normally, there is a trade-off between low NO_x emissions and low UHC emissions. This means that if the engine operation is changed in order to reduce NO_x emissions higher UHC emissions will often be a negative side effect.

Furthermore, it is well known that the electrical efficiency of the CHP engines is affected by varying engine settings.

In order to examine how much emissions and efficiencies are affected by varying engine settings measurements have been conducted on different natural gas fired engine based on CHP units in Denmark.

The participants in the project are:

- Rolls Royce
- Wärtsila

- National Environmental Research Institute, DMU
- Danish Gas Technology Centre, DGC.

The measurements have been conducted by Kim Larsen (Rolls Royce), Morten Hansen (Wärtsila) Lars Jørgensen and Steen D. Andersen (DGC).

The project was financially supported by Energinet.dk as a part the PSO ForskEL programme.

2 Conclusions

The emissions of NO_x, CO and UHC as well as the composition of the hydrocarbon emissions were measured for four different stationary lean burn natural gas fired engines installed at different combined heat and power (CHP) units in Denmark. The units have been chosen to be representative for the natural gas engine based on power production in Denmark.

The NO_x emissions were varied from around 200 to 500 mg/m^3(n) by varying the ignition timing and the excess of air.
For each of the examined engines measurements were conducted at different combinations of ignition timing and excess of air.

The measurements showed the NO_x emissions were relatively more sensitive to engine setting than UHC, CO and formaldehyde emissions. By reducing the NO_x emissions to 40 % of the initial value (from 500 to 200 mg/m^3(n)) the UHC emission were increased by 10 % to 50 % of the initial value.
The electrical efficiency was reduced by 0,5 to 1,0 % point.

Examined engines

Four different natural gas fired engines have been chosen for measurement of emissions as well as electrical and heat efficiency. The four engines are in operation on four different combined heat and power plants (CHP) in Denmark. Make and size of the engine are given in Table 1. They are all pre-chamber engines.

Table 1. Make and size of the examined engines.

Unit	Make	Size
#1	Rolls Royce B35:40	4990 MW_e
#2	Rolls Royce KVGS-G4	2075 MW_e
#3	Wärtsilä V25SG	3140 kW_e
#4	Wärtsilä V34SG	6060 kW_e

The engines are selected in order to be representative for the natural gas engine based on CHP production in Denmark. The engine at unit #1, the Rolls Royce B35:40, is a relatively new type of engine. The other three engines are commonly used on CHP units. The four examined engine type makes out around 40 % of the total natural gas consumption on natural gas engine based on CHP units in Denmark.

2.1 Operation conditions

For all four engines emissions and efficiency were measured at different combinations of excess of air (λ) and ignition timing (IT). The excess of air and the ignition timing were set so the following NO_x emission levels were obtained:

500, 400, 300, and 200 mg/m^3(n), ref. 5 % O_2

For each of the examined operational conditions the following measurements were conducted:

- O_2, CO_2, CO, NO_x, NO_2, UHC (by FID)
- Natural gas consumption, heat and electricity production
- Hydrocarbon composition (by FTIR), including formaldehyde.
- For each engine 2-3 samples were collected for GC analysis

The engine settings were chosen by the engine supplier. It was done so it fits the scheme shown in Table 2. As shown in the table four measurements with fixed excess of air and fixed time of ignition and four measurements with fixed time of ignition and different excess of air are carried out. However, for one of the engines it was only possible to obtain steady operation at seven of the eight chosen engine settings.

Table 2. Examined operational conditions. TI denotes the time of ignition, M is numeration of individual measurements.

Unit: $mg/m^3(n)$ @ 5 % O_2	TI_1	TI_2	TI_3	TI_4
λ_1			M_5 $NO_x = 200$	
λ_2			M_6 $NO_x = 300$	
λ_3	M_1 $NO_x = 200$	M_2 $NO_x = 300$	$M_{3/7}$ $NO_x = 400$	M_4 $NO_x = 500$
λ_4			M_8 $NO_x = 500$	

3 Measurements

Measurements of emissions were carried out using different measurement techniques. The applied measurement techniques as well as obtain results are described in the following.

The effect of varying the two parameter excess of and ignition timing individually is shown in Figure 1.

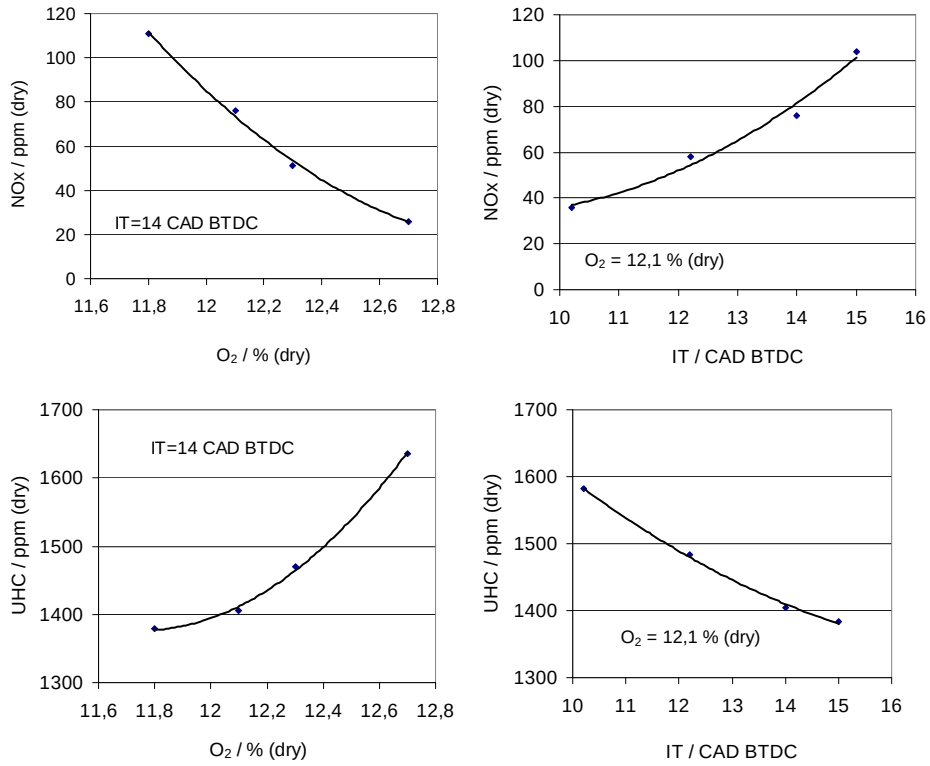


Figure 1. The effect of variation of excess of air and ignition timing. Unit #3. IT: Ignition Timing; CAD BTDC: Crank Angle Degree Before Top Dead Centre.

3.1.1 Formaldehyde measurements

The reference method for analysis of measuring formaldehyde concentration in flue gas is to use impingers containing an aqueous solution of DNPH[1] absorbent followed by HPLC[2] analysis. However, this is a time demanding and expensive measurement which doesn't provide real time information of the formaldehyde content. Therefore it was decided to use the FTIR instrument for the formaldehyde measurements and additionally perform some impinger measurements for comparison. The comparison is given in Figure 2.

[1] Dinitrophenylhydrazine
[2] High performance liquid chromatography (or high pressure liquid chromatography)

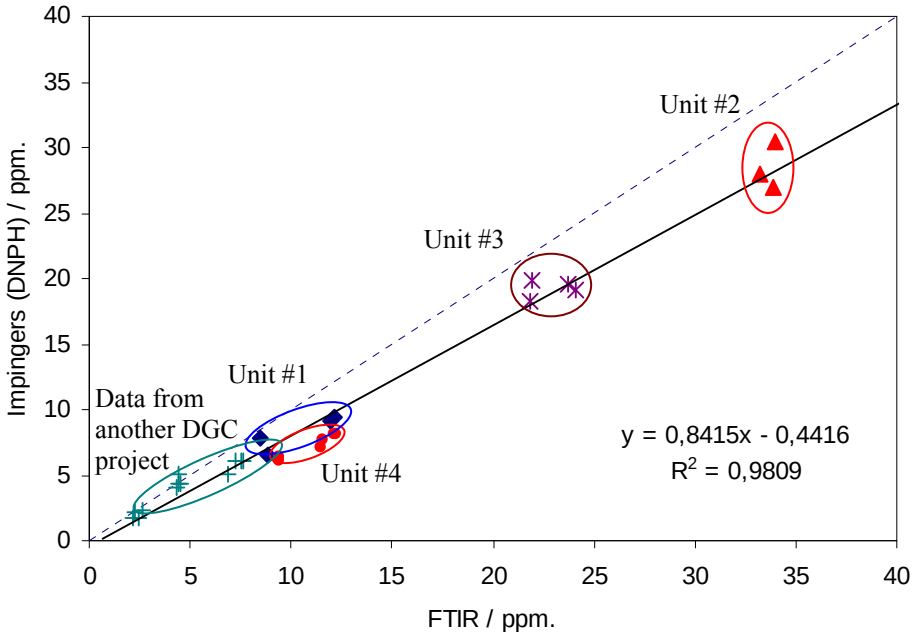


Figure 2. Comparison of formaldehyde measured using different techniques.

The reference method seems to under estimate the formaldehyde content compared to the FTIR method. However, each measuring method is subject to a certain degree of uncertainty, and there are no decisive reasons to discard the results obtained by the FTIR instrument. Therefore the results from the FTIR will be used in the further evaluations.

3.1.2 Assessment of CO, UHC and NO_x measurements

The components CO, NO_x and UHC were measured by both FTIR and the respective reference methods. The reference method for CO measurements is to use a NDIR (Non Dispersive Infra Red) sensor, the reference method for NO_x measurements is to use a CLD (chemiluminescence detector) instrument and the reference method for UHC measurements is to use a FID (flame ionisation detector). FID instruments are also referred to as C-counters as the output signal is proportional to the concentration of hydrocarbon present in the sample gas. A comparison between the conducted measurements is given in Figure 3 for engine unit #1. Similar figures for all examined engines are given in Appendix A.

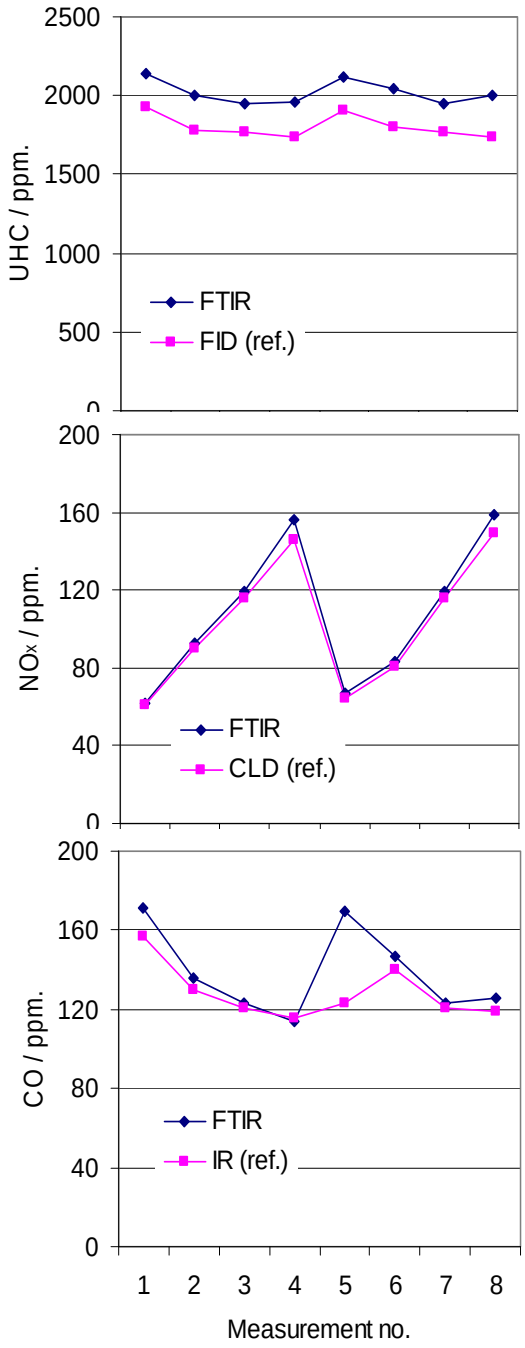


Figure 3. Comparison of FTIR measurement with referent methods for UHC(measured as C_1), NO_x and CO. Engine unt #3.

It is indicated that the FTIR instrument is able to determine the CO and the NO_x in the flue gas with satisfying accuracy.
The given UHC values are the concentration of C-atoms bounded as hydrocarbons. That is determined as

$$UHC_{FTIR} = 1 \cdot C_{CH_4} + 2 \cdot C_{C_2H_6} + 3 \cdot C_{C_3H_8} .....$$

where C is the concentration measured by FTIR. It is seen that the UHC concentration determined by FTIR is around 10 % higher than concentration determined the reference method.

3.1.3 Composition of UHC emissions

The reference method for measuring UHC emissions is as mentioned FID measurement. However, it only gives the total concentration of hydrocarbons in the flue gas.
As FID is the reference method and the instrument is calibrated using a certified test gas before and after each set of measurements the FID measurements are believed to be closer to the true concentration than the FTIR measurements. Therefore, the FID measurements are a measure for the total concentration of UHC and the FTIR measurements are used for determining UHC composition.
The corrected concentration of the hydrocarbon component (C_i) is determined as

$$C_i(Corrected) = C_i(FTIR\,as\,measured)\frac{C_{UHC}(FID, ref, as C_1)}{C_{UHC}(FTIR, as\,C_1)}$$

For assessing the quality of the hydrocarbon composition determined by FTIR samples of flue gas were collected and analysed by a gas chromatograph (GC) at DGC's laboratory.

An example of this corrected hydrocarbon composition is given in Table 3 together with the composition measured by FTIR, GC and the reference FID measurement. It is shown that according to both the GC and the FID measurements the UHC concentration given as C_1 equivalents is 1286 ppm. That is, however, a coincidence as the accuracy on both of the two measurements is around ± 5 %.

Table 3. Hydrocarbon composition for unit #1 (measurement 5).

Unit (ppm.)	**GC**	**FTIR** (as measured)	**FTIR** (Corrected)	**FID** (reference method)
Metan	1048	1255	1097	
Ethen	4,6	5,81	5,1	
Ethan	65,2	51,7	45,2	
Propen	0	*	0	
Propan	26,5	29,8	26	
i-butan	0	*	*	
n-butan	2,4	0	*	
Other C_4	0	*	*	
i-pentan	1,1	*	*	
n-pentan	0,8	*	*	
Total	1149	1342	1173	
C_1 eq.	1286	1471	1276	1286

The hydrocarbon composition in the flue gas for all examined operation condition for engine unit #1 is given in Figure 4. The figure indicates that the concentration of hydrocarbons decreases with increasing NO_x emission. The hydrocarbon composition for all engine units is given in Appendix B. The relative hydrocarbon composition (given as fraction of the total hydrocarbon concentration) is shown in Figure 5 and it is shown that it is practically the same for all examined operation conditions.

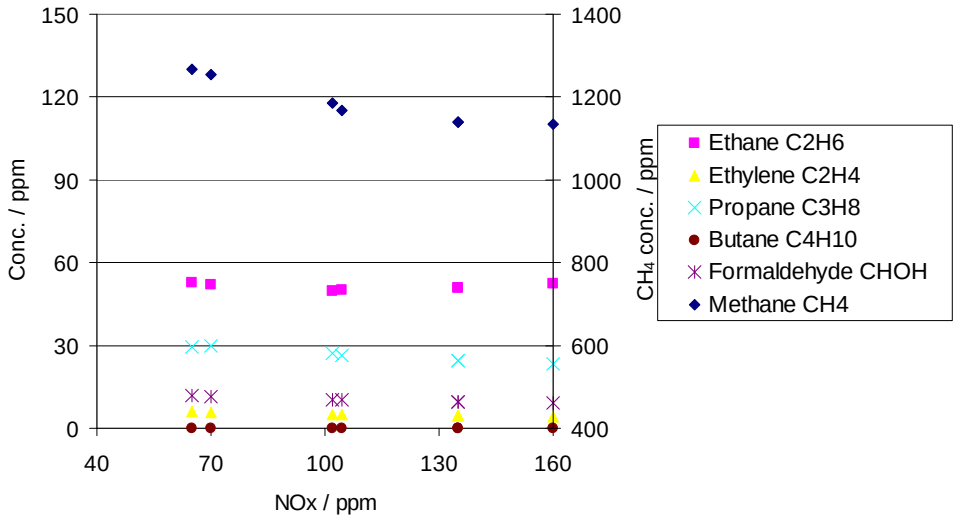


Figure 4. Composition of unburned hydrocarbons measured by FTIR. Engine unit #1.

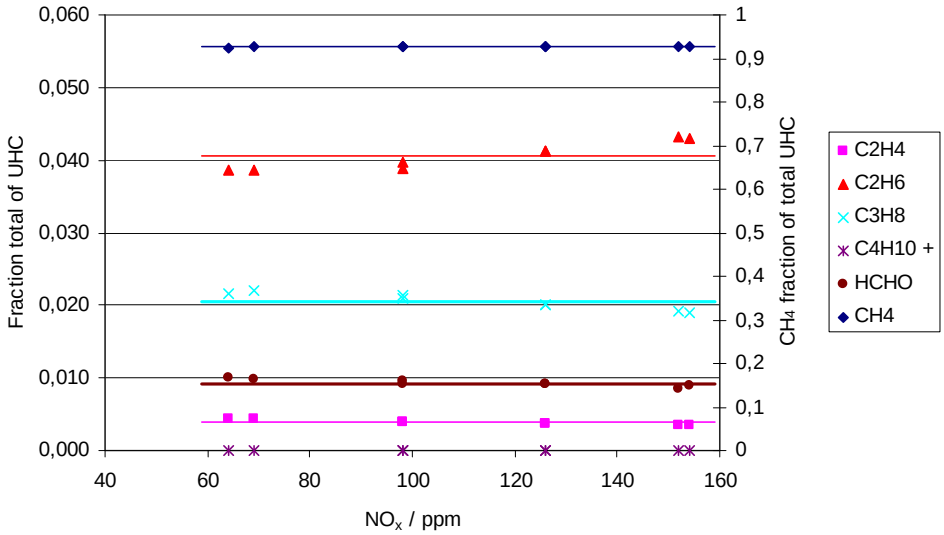


Figure 5. Relative UHC composition for the examined engine settings for engine unit #1. The lines represent the average of examined settings.

The compositions of the hydrocarbon emissions for the four examined were compared with each other and with the hydrocarbon composition of natural gas. See Figure 6. For all four engines it is shown that the hydrocarbon composition is close to the composition of natural gas. Generally, it is seen that methane fraction in the exhaust gas for all four engine is slightly higher than the methane fraction in the natural gas relative to the total hydrocarbon concentration. That is because the methane molecules are relative stable compared to the other hydrocarbons and therefore a relatively smaller fraction of the methane molecules will be oxidised compared to the higher hydrocarbons. Similar results regarding the UHC composition were reported earlier [1]. Here it was reported that the butane fraction of the total hydrocarbon in flue gas from lean burn natural gas engines was around 50 % lower that the butane fraction in natural gas. This indicates that the true butane emissions are higher than what was measured by FTIR.

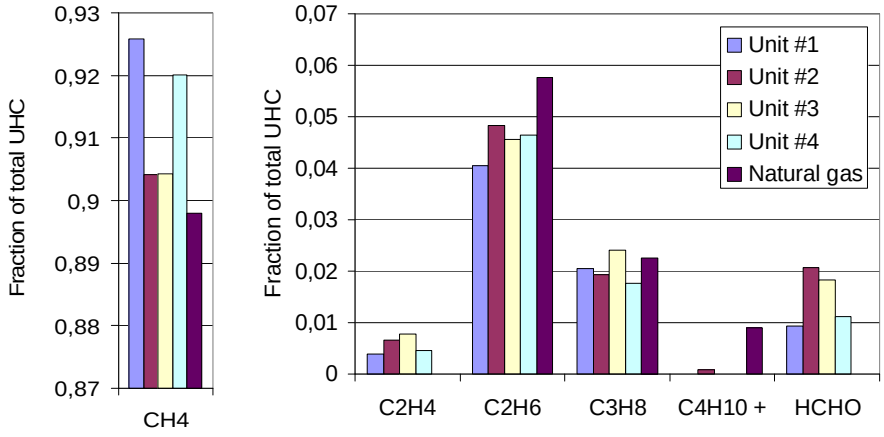


Figure 6. Average UHC composition for the examined engine units (determined by FTIR) together with the natural gas composition.

3.1.4 Regulated emissions and efficiencies

In this section the measured concentration of the regulated species CO, NO_x and UHC are presented together with the obtained heat and electrical efficiencies for the four examined engines. See Figure 7 to Figure 10. The efficiencies and the emissions of CO and UHC are all shown as a function the NO_x emissions.

The obtained results are as expected for all engine.

- UHC emissions decrease with increasing NO_x emissions
- CO emissions decrease with increasing NO_x emissions
- The electrical efficiency increases with increasing NO_x emissions

From Figure 7 to Figure 10 it can be seen that by reducing the NO_x emissions by a factor of 2,5 the UHC emissions were increased by 10 – 50 %. Furthermore, it is seen that the CO emissions are slightly more sensitive to engine settings than the UHC emissions.
The reason for the very low CO emissions is that all engines are equipped with CO catalysts.

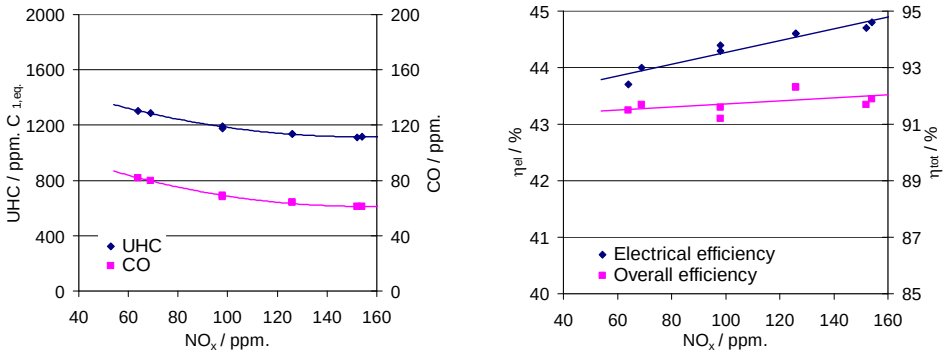


Figure 7. Emissions and efficiencies for the examined engine settings. Unit #1.

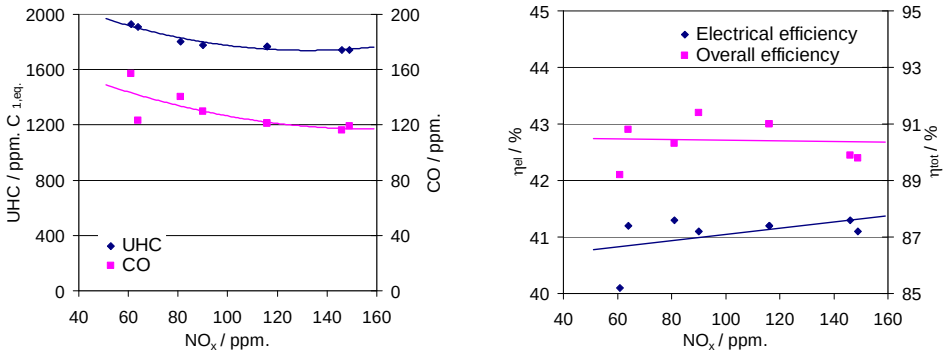


Figure 8. Emissions and efficiencies for the examined engine settings. Unit #2.

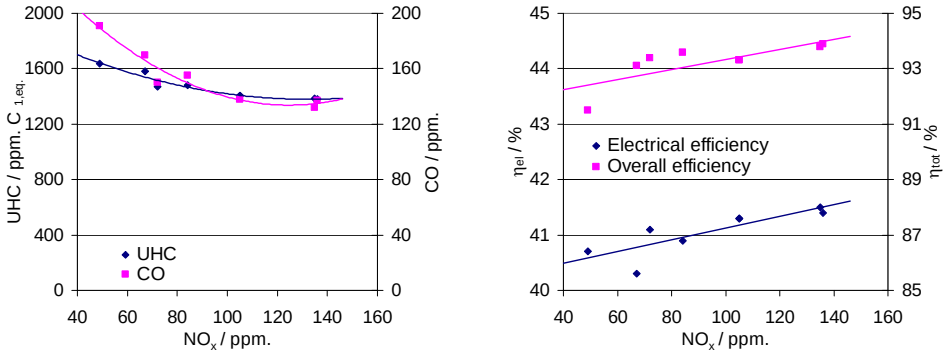


Figure 9. Emissions and efficiencies for the examined engine settings. Unit #3.

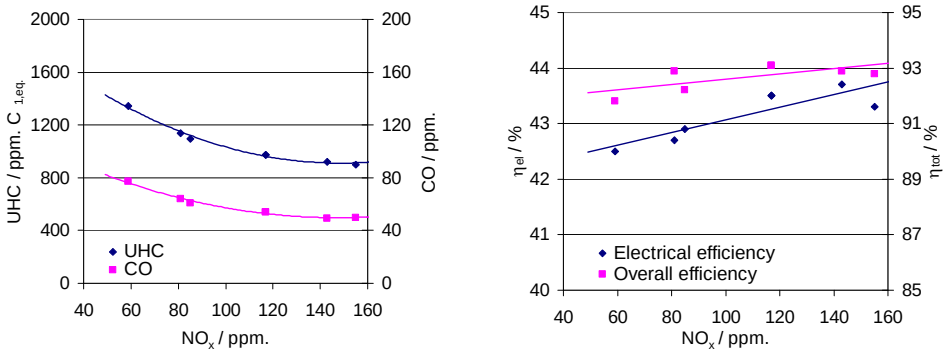


Figure 10. Emissions and efficiencies for the examined engine settings. Unit #4.

4 Conversion of concentration to mass flow

In order to be able to determine the harmfulness of the exhaust gas it is not enough to know the actual concentration of the different species. Also the total flow of exhaust gas must be known in order to determine the amount emitted. From the measured fuel and exhaust gas compositions as well as fuel consumption the exhaust gas flow can be determined.

Complete combustion of natural gas can be described as

$$NG + \lambda\, AF_{stoic}\left(O_2 + 3{,}76N_2\right) \longrightarrow X_{CO2}CO_2 + X_{H_2O}H_2O + \left(\lambda - 1\right)AF_{stoic}O_2 + \lambda\, AF_{stoic}\,3{,}76N_2 \qquad \text{R 1}$$

Where

NG is natural gas

AF_{stoic} is the stoichiometric air-fuel ratio (mole/mole)

X_{CO2} is the amount of CO_2 produced by combustion of one mole of natural gas

X_{H_2O} is the amount of H_2O produced by combustion of one mole of natural gas.

The volume flow of exhaust gas can be determined as

$$\dot{V}_{exhaust} = \dot{V}_{NG} \cdot \frac{V_{exhaust}}{V_{NG}}$$

Where

$\dot{V}_{exhaust}$ is the volume flow of exhaust gas

$\dot{V}_{NG}$ is the measured consumption of natural gas (volume)

$\frac{V_{exhaust}}{V_{fuel}}$ is a term that describes the volume ratio between formed exhaust gas and fuel consumption. In real combustion processes the combustion does not occur as described by R1. CO and NO_x are formed and a fraction of the fuel remains partly unburned and will be present in the exhaust gas as UHC emission. Therefore it is necessary to apply an expression that takes the measured concentrations of CO, UHC and NO_x emissions into account. Such expression is described in [2].

$$\frac{V_{exhaust}}{V_{fuel}} = \left(4{,}76\left(X_{CO_2}\left(1 + {Y_{O_{2,eq}}}/{Y_{CO_{2,eq}}} \right) + ½ X_{H_2O} \right) + 1 - X_{H_2O} \right) \frac{0{,}5}{0{,}5 - Y_{UHC}}$$

Where

$$Y_{CO_{2,eq}} = Y_{CO_2} + Y_{CO} + Y_{UHC}$$

$$Y_{O_{2,eq}} = Y_{O_2} - 0{,}5Y_{CO} - \left(1 + \frac{{H}/{C}_{fuel}}{4} \right) Y_{UHC} + Y_{NO_x}$$

$Y_{CO_2,}$ Y_{CO} and Y_{UHC} are the measured volume fraction of the species in the exhaust gas. ${H}/{C}_{fuel}$ is the molar ratio between hydrogen and carbon atoms in the fuel. For further details, please refer to [2].

The mass flow of the measured species from the engines is given in Appendix D

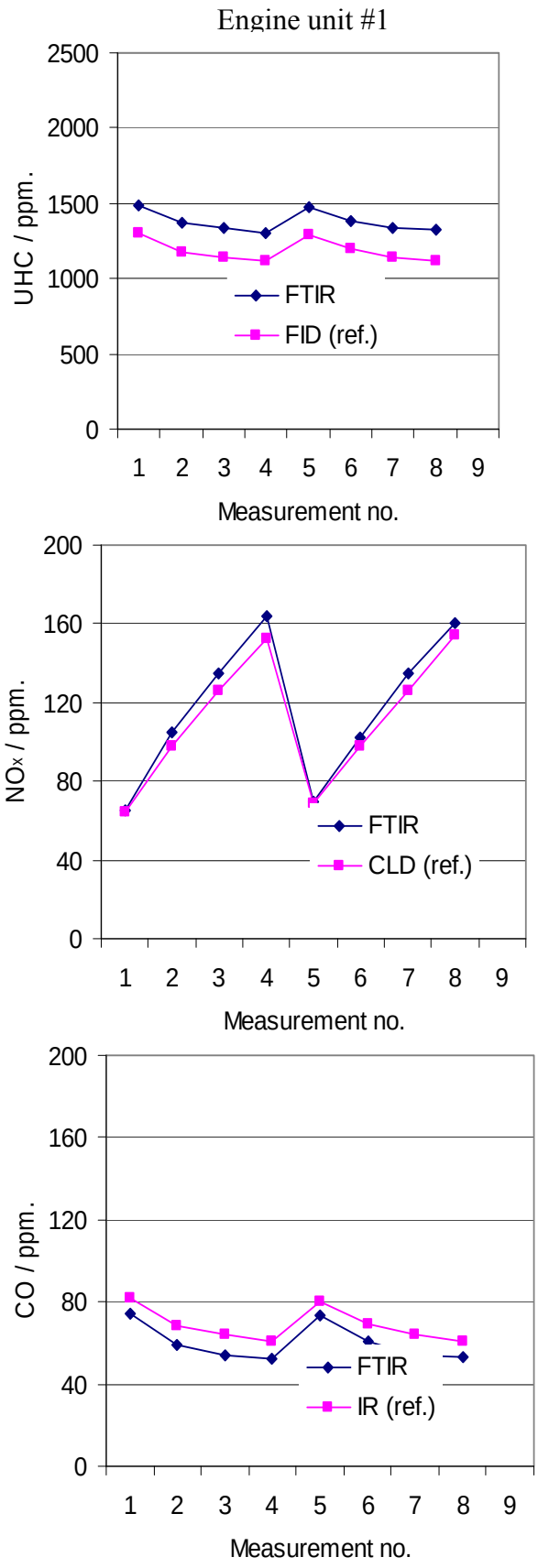
5 References

[1] Kortlægning af emissioner fra decentrale kraftvarmeværker (Mapping of emissions from decentral combined heat and power plants. In Danish) . Delrapport 4. ISBN 87-7795-237-5. DGC-rapport April 2003.

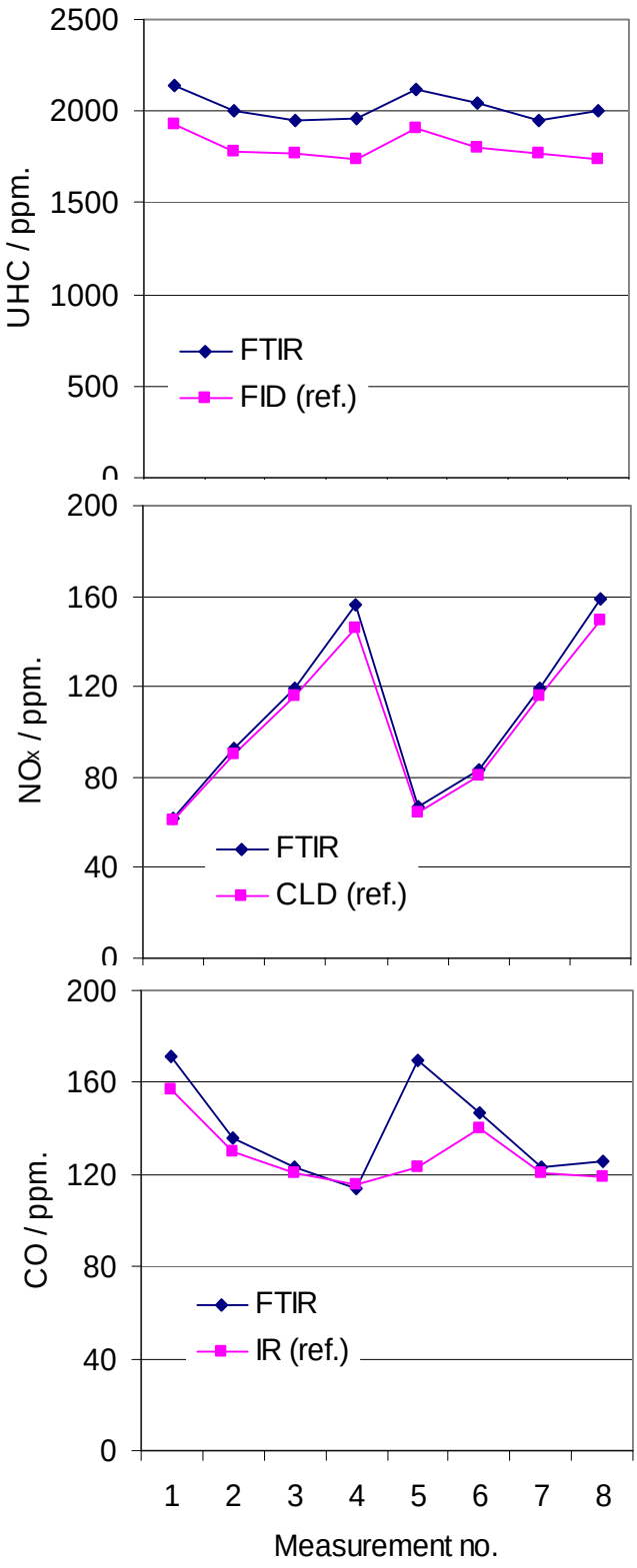
[2] Faster CHP gas engine start with less emission. An analysis of emissions during start and stop of natural gas engines, state of art 2005/2006. ISBN 87-7795-301-0. DGC report. 2007.

Appendix A

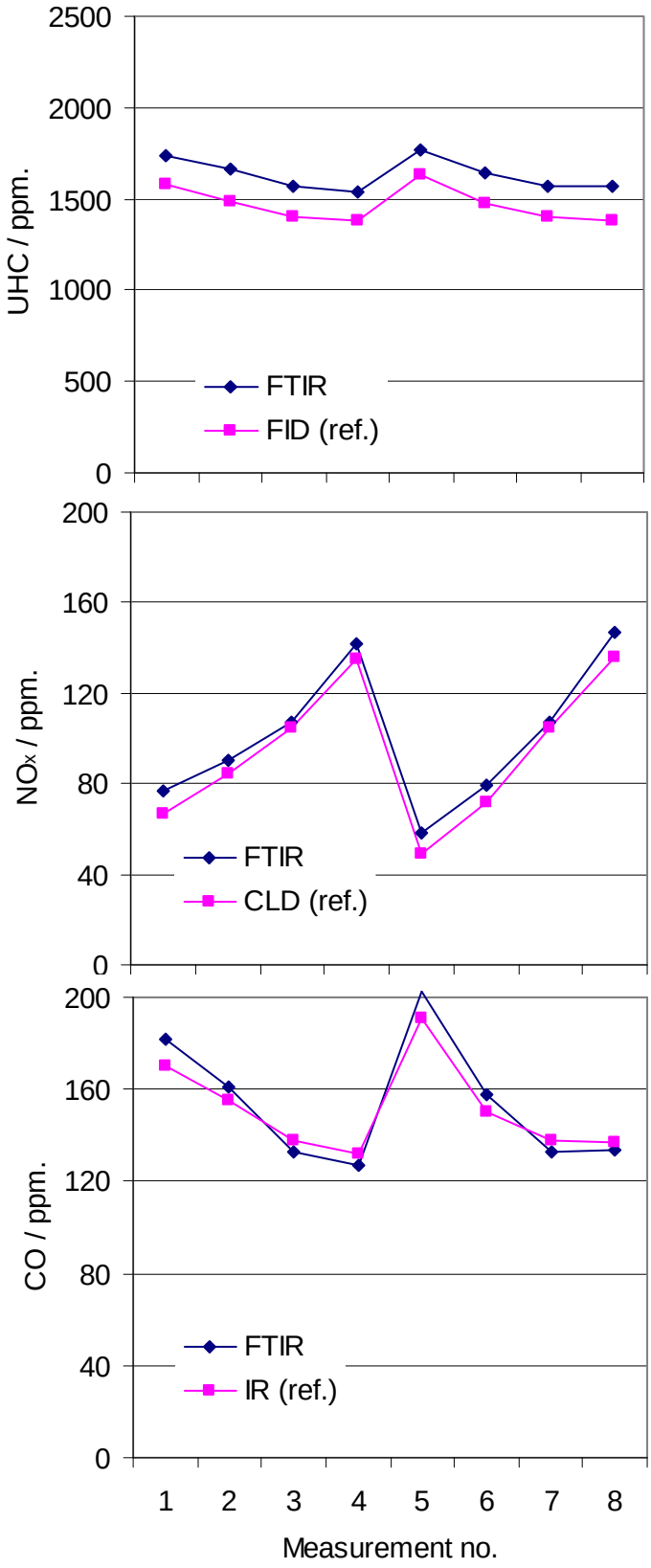
Comparison of FTIR measurement with referent methods for UHC (measured as C_1), NO_x and CO.



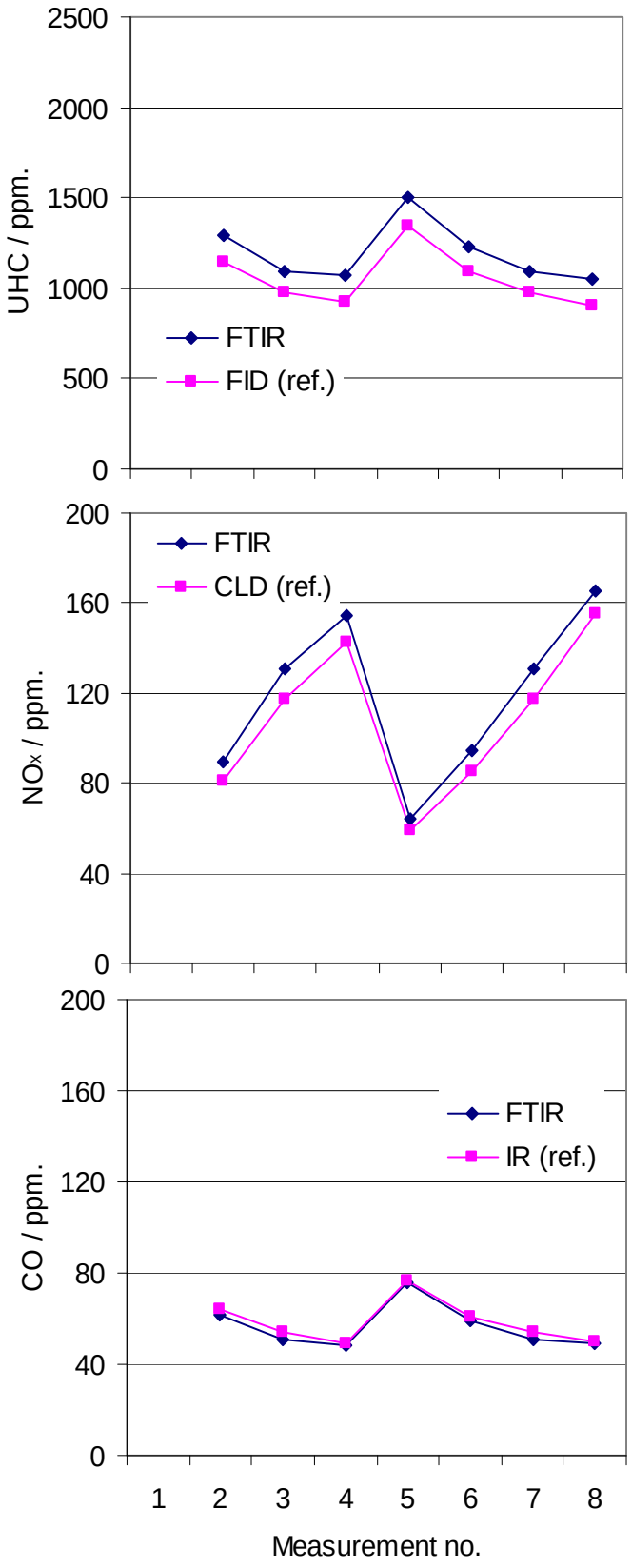
Engine unit #2



Engine #3


2500
2000
1500
1000
500
0
UHC / ppm.
FTIR
FID (ref.)
200
160
120
80
40
0
NOx / ppm.
FTIR
CLD (ref.)
200
160
120
80
40
0
CO / ppm.
FTIR
IR (ref.)
1
2
3
4
5
6
7
8
Measurement no.

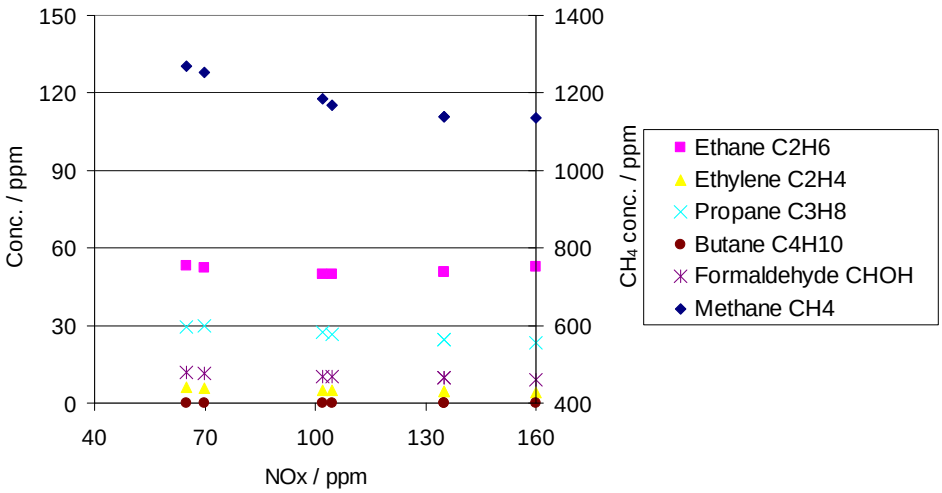
Engine unit #4



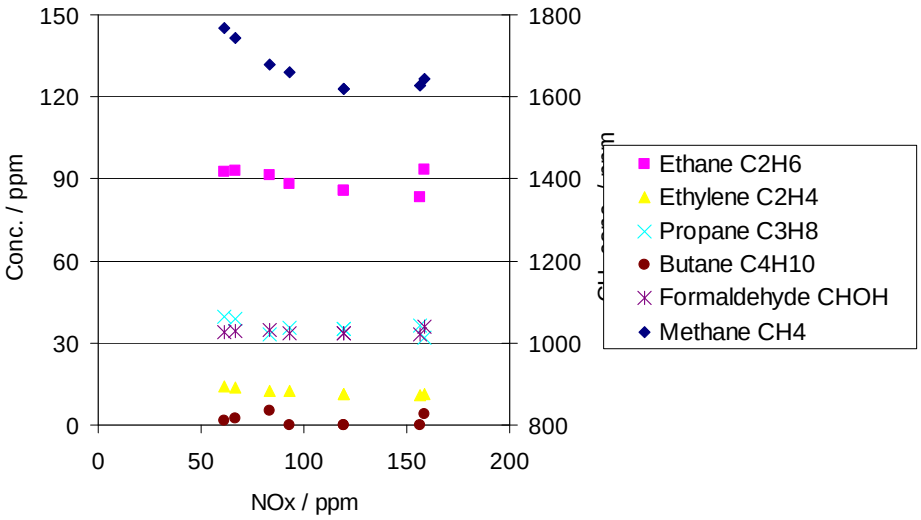
Appendix B

Composition of unburned hydrocarbons measured by FTIR/FID

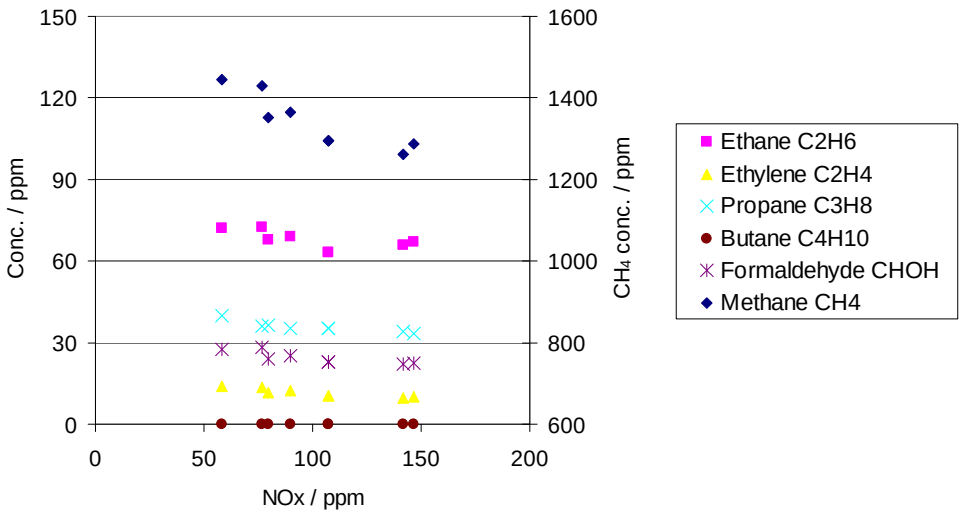
Engine Unit #1



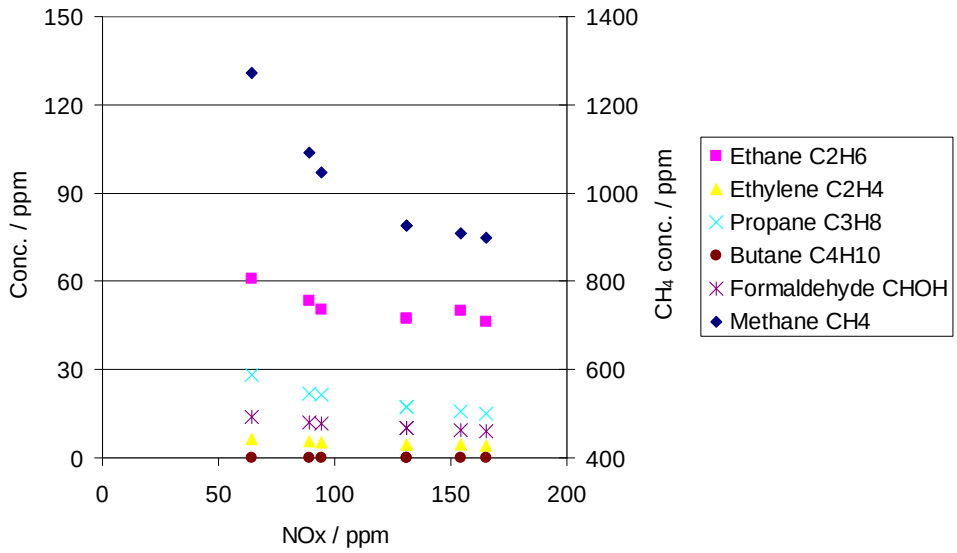
Engine Unit #2



Engine Unit #3

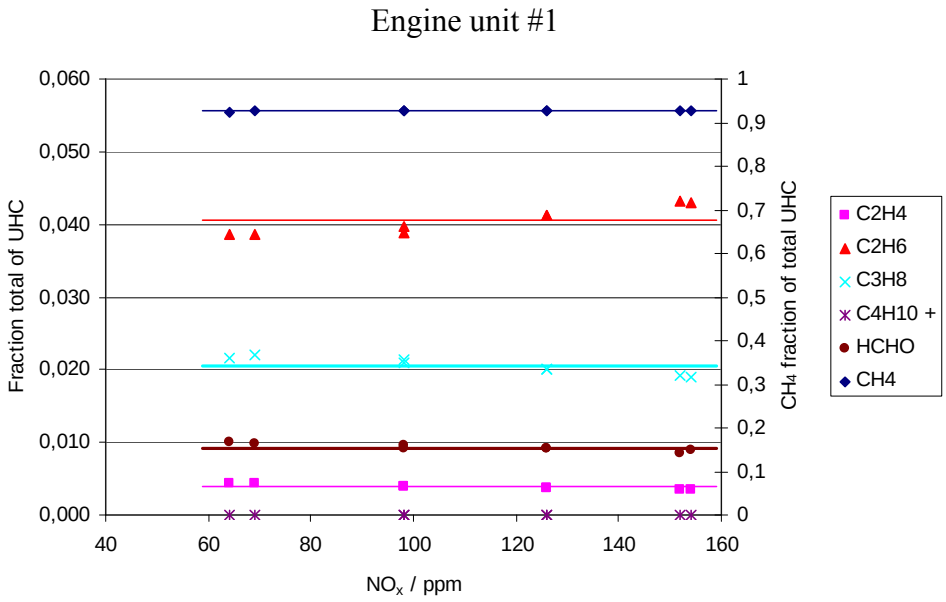


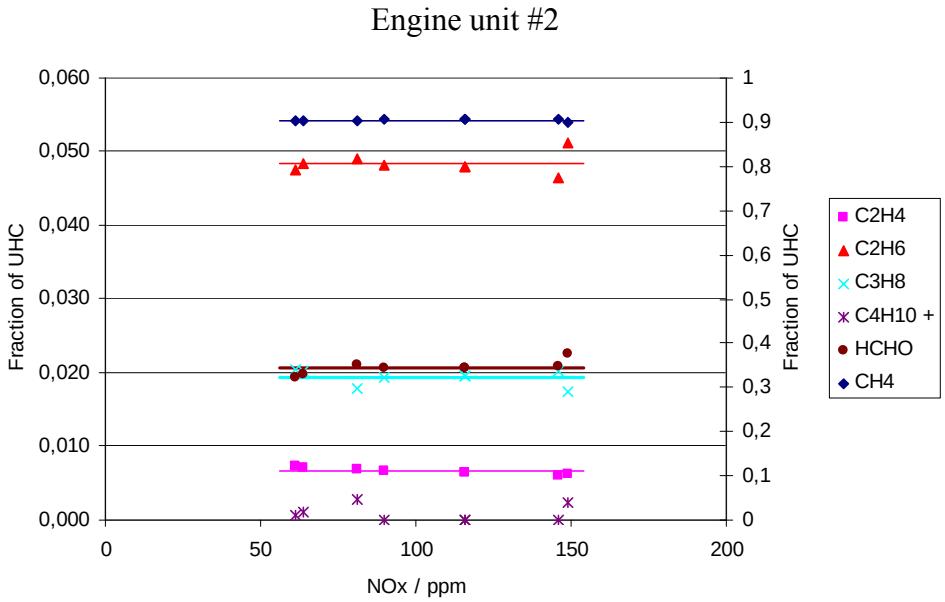
Engine Unit #4



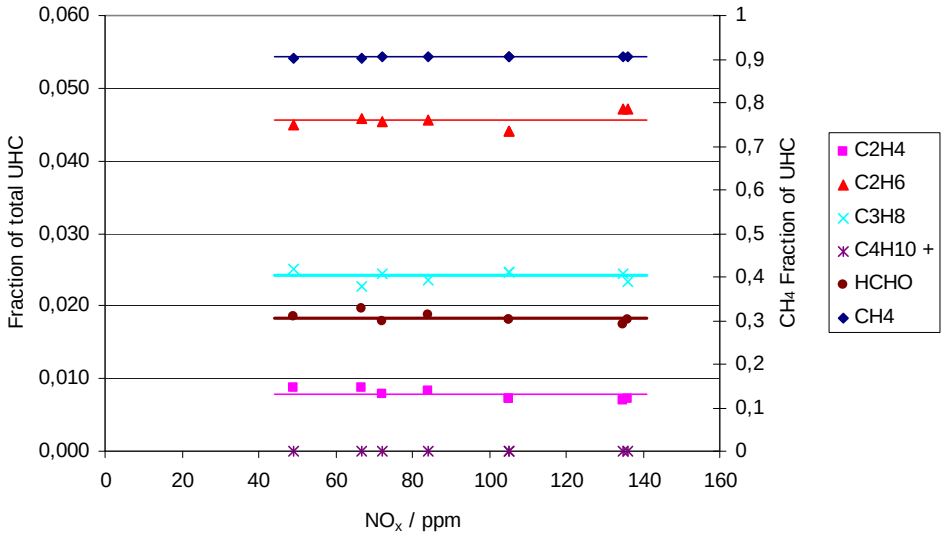
Appendix C

Relative UHC composition for the examined engine settings for all engine unit. The lines represent the average of examined settings.

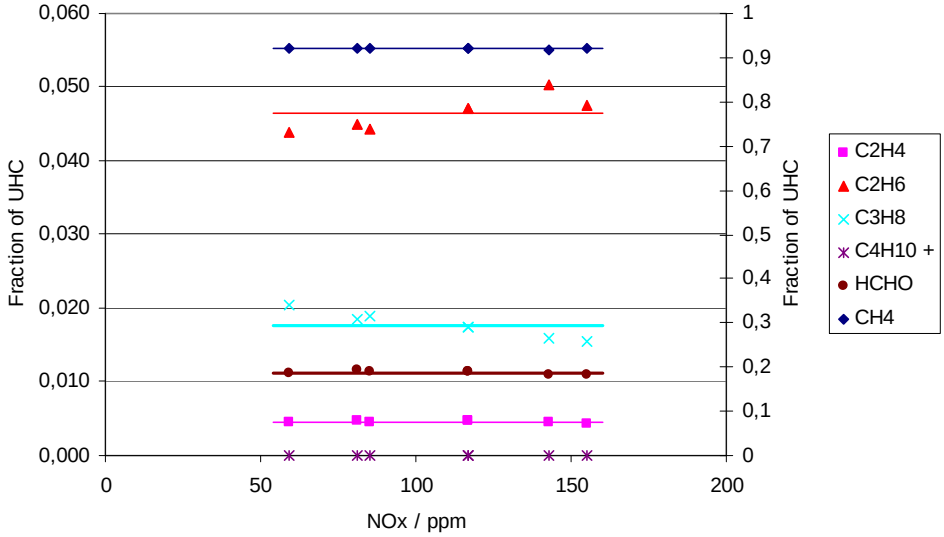




Engine unit #3



Engine unit #4



Appendix D

Determined mass flow of the different measured species out of the examined engines.

		Measurement							
Unit #1		#1	#2	#3	#4	#5	#6	#7	#8
CH4	mg/s	4823	4266	4052	3937	4785	4338	4052	3892
C2H4	mg/s	40	31	28	26	39	32	28	25
C2H6	mg/s	378	342	339	345	374	341	339	338
C3H6	mg/s	-	-	-	-	-	-	-	-
C3H8	mg/s	278	238	216	201	282	248	216	196
C4H10 +	mg/s	0	0	0	0	0	0	0	0
HCHO	mg/s	88	74	67	61	85	73	67	63
NO	mg/s	307	486	694	843	354	516	694	768
NO2	mg/s	246	329	290	331	237	286	290	441
N2O	mg/s	0	0	0	0	0	0	0	0
CO	mg/s	559	454	419	396	550	462	419	390
CO2	mg/s	59	58	58	57	58	58	58	57
O2	mg/s	88	85	82	81	90	86	82	79
Exhaust gas	m3(n)/s	6,053	5,933	5,821	5,785	6,098	5,942	5,821	5,696

		Measurement							
Unit #2		#1	#2	#3	#4	#5	#6	#7	#8
CH4	mg/s	3217	2891	2831	2777	3169	2930	2831	2705
C2H4	mg/s	46	38	35	32	43	39	35	32
C2H6	mg/s	316	288	281	267	318	299	281	288
C3H6	mg/s	-	-	-	-	-	-	-	-
C3H8	mg/s	199	169	169	171	194	159	169	144
C4H10 +	mg/s	9	0	0	0	15	33	0	25
HCHO	mg/s	128	123	121	119	130	128	121	127
NO	mg/s	117	205	281	373	132	185	281	393
NO2	mg/s	174	191	210	231	168	176	210	206
N2O	mg/s	2	0	0	0	2	2	0	1
CO	mg/s	554	445	407	389	434	484	407	393
CO2	mg/s	29	29	29	28	29	29	29	29
O2	mg/s	47	45	44	43	47	46	44	42
Exhaust gas	m3(n)/s	2,821	2,739	2,693	2,680	2,818	2,762	2,693	2,644

		Measurement							
Unit #3		#1	#2	#3	#4	#5	#6	#7	#8
CH4	mg/s	4093	3843	3618	3481	4490	3856	3618	3475
C2H4	mg/s	69	61	50	47	76	58	50	48
C2H6	mg/s	389	364	330	340	419	363	330	339
C3H6	mg/s	-	-	-	-	-	-	-	-
C3H8	mg/s	283	274	272	259	342	286	272	248
C4H10 +	mg/s	0	0	0	0	0	0	0	0
HCHO	mg/s	166	149	135	126	173	142	135	130
NO	mg/s	212	342	444	597	163	304	444	636
NO2	mg/s	280	235	260	273	221	192	260	220
N2O	mg/s	0	0	0	0	0	0	0	0
CO	mg/s	934	853	753	707	1118	836	753	733
CO2	mg/s	44	43	43	43	43	43	43	43
O2	mg/s	75	76	75	73	85	78	75	72
Exhaust gas	m^3(n)/s	4,394	4,400	4,364	4,284	4,681	4,457	4,364	4,279

		Measurement							
Unit #4		#1	#2	#3	#4	#5	#6	#7	#8
			mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3
CH4	mg/s		5353	4450	4180	6446	5130	4450	4091
C2H4	mg/s		49	39	35	56	44	39	34
C2H6	mg/s		491	427	430	577	463	427	396
C3H6	mg/s		-	-	-	-	-	-	-
C3H8	mg/s		295	230	199	392	289	230	189
C4H10 +	mg/s		0	1	0	0	0	1	0
	mg/s								
HCHO	mg/s		126	103	94	147	119	103	90
NO	mg/s		622	877	1084	435	640	877	1086
NO2	mg/s		334	463	538	293	364	463	703
N2O	mg/s		0	0	0	0	0	0	0
CO	mg/s		619	508	459	762	588	508	465
CO2	mg/s		81	80	79	81	80	80	80
O2	mg/s		127	122	122	133	127	122	119
Exhaust gas	m3(n)/s		7,737	7,524	7,492	7,919	7,706	7,524	7,442