Formaldehyde reduction by catalyst

Full-scale field test on gas engines

Project Report
PSO project 5230

February 2007

Formaldehyde reduction by catalyst

Full-scale field test on gas engines

Per G. Kristensen

Table of Contents   **Page**

Appendices

1   Preface

This report presents the results of a field test of commercially available catalysts for formaldehyde reduction on gas engine exhaust. The project has been performed by Danish Gas Technology Centre (DGC) in collaboration with the Danish natural gas engine suppliers. The engine suppliers have participated at their own cost in the project and have equipped the gas engines with catalyst. *Rolls Royce Denmark* participated with the *Tørring* plant. *Pon Power* participated with the *Hjortebjerg* plant. *GE-Jenbacher* participated with the *Jetsmark* plant. *GE-Jenbacher* has kindly allowed results from a catalyst test at *Frederiks* to be included in this work.
Wärtsilä Denmark participated without a test plant since it was not possible to find a suitable test plant within the framework of this project. DGC wishes to acknowledge the support from the engine suppliers and the plant owners to the project.

The emission performance and documentation project was organised partly as a gas company project and partly as a PSO project. DGC wishes to acknowledge the financial support from Eltra PSO (contract no. 5230) and FAU GI (project no. 725.40).

The field test program was supported by an expert monitoring group from the above mentioned engine suppliers, the Danish EPA, The Danish plant owners' organisations, catalyst suppliers and the gas companies' Technical Committee for Utilisation and Installation (FAU GI) and from Energinet.dk. Contact information for participants in project meeting can be found in Appendix A. DGC wishes to acknowledge the contribution from these organisations.

Steen Andersen and Henrik Andersen, DGC, have performed all emission measurements. Individual emission test reports are available for all emission data in this project. The draft report has been submitted for comments among the project participants and interested organisations (Appendix A).

Per G. Kristensen   Jan K. Jensen
Project Manager   Executive Vice President

2   Summary

Direct oxidation catalyst for formaldehyde reduction in engine exhaust gases seems to be the best available technology for formaldehyde reductions considering the reduction efficiency, investments cost, and low overhead and maintenance cost.

Two types of catalyst have been tested in field conditions for approximately two years of operation, accumulating from 5.500 to 12.500 hours of operation with good results.

The two-year test period can be considered to be short compared to the normal operation time span for other catalysts from 20-40.000 hours. However – giving the two-year time span for testing, and the engine operation pattern in Denmark, 10.000 hours of operation is what is possible within the framework of the Danish EPA exemption time of three years total.

The catalyst supplied from Johnson Matthey showed the best oxidation results starting with a 95 % reduction of formaldehyde decreasing to 85 % reduction of formaldehyde at 5.500 and 12.500 hours of operation. The catalyst was tested at site Hjortebjerg and site Frederiks. The last site was not directly part of the project, but GE-Jenbacher kindly provided the exhaust results to the project.

The second catalyst tested was supplied by Süd-Chemie. This catalyst was tested at site Jetsmark and site Tørring. This catalyst showed approximately 60 % reduction at the beginning decreasing to approximately 40-45 % reduction at 10.000 hours of operation.

At project meetings, where the field-test results were discussed, both catalyst suppliers have confirmed that it will be technically possible to provide catalysts that can reduce emissions to the desired emission level. The costs of catalyst and installation will of course increase as the desired emission level becomes lower.

Both types of catalyst are capable of reducing other emission components. The otherwise problematic acetaldehyde and acrolein are largely removed by the catalysts, and CO emission will become much lower than demanded

by emission standards using formaldehyde catalysts. The emission of odour is reduced by approximately 40 %, but large variations are present in the results.

Emission of unburned hydrocarbons will not be significantly reduced by the use of formaldehyde catalyst. The main components of the unburned hydrocarbon are the natural gas constituents, methane, ethane and propane, which were only slightly reduced during the period of catalyst operation. A part reduction was observed for non-saturated hydrocarbons.

Temperatures were monitored through the field-test period by sampling exhaust gas temperatures before and after the catalyst in order to clarify if the catalyst occasionally was exposed to severe temperature conditions. This was not the case for any of the three catalysts during the test period.

Natural gas engines in Denmark start and stop many times a year putting some thermal stress on the catalyst, but there was no observation of extreme high temperatures. The normal cycles of operation will follow the sequence: Engine start and increased exhaust gas temperatures during approximately 15 minutes. Stable exhaust temperatures in the typical range from 400 to 450 °C during normal operation followed by an engine cool down period before termination of operation. During the engine cool down period of 10-15 minutes the exhaust gas temperature will increase 60-80 °C.

Other methods for formaldehyde reduction exist; they have been reported separately and the methods have only been summarised here. The main conclusion on the other methods is that at present conditions (for energy prices) the other methods will be less efficient and/or more costly to install and operate.

Using the catalyst experience obtained in this study, and extrapolating to a higher number of operation hours, it has been estimated that the majority of the Danish gas engines will be able to comply with an emission target of 20 mg/m^3 @ 5 % O_2 and 30 % efficiency. The extrapolation is primarily sensitive to the rate of decay on catalyst activity at higher operation hours.

3   Extended summary in Danish

Direkte brug af oxidationskatalysatorer til fjernelse af formaldehyd fra gasmotorrøggas ser ud til at være den mest lovende teknik, når der tages hensyn til de opnåede emissionsreduktioner og værkernes omkostninger til investering og fremtidige drift.

Miljøstyrelsen fremsatte i Luftvejledningen /3/ i 2001 en emissionsgrænse-værdi på 10 mg/m^3 ved 5 % O_2 ved en virkningsgrad på 30 %. Grænsevær-dien ændres ligefrem proportionalt i op- og nedadgående retning afhængig af elvirkningsgraden for nye gasmotoranlæg med en samlet indfyret effekt større end 5 MW. Reglen skulle træde i kraft den 1. juli 2003.

Grænseværdien blev fremsat, fordi Miljøstyrelsen var blevet opmærksom på, at der forekommer betydelige emissioner af formaldehyd fra gasmoto-ranlæg i Danmark. Formaldehyd er efter Luftvejledningen grupperet som et Hovedgruppe 1 stof, der for anden industri reguleres med en generel emissi-onsgrænseværdi på 5 mg/m^3 (10 % O_2), dog med en undtagelse for mineral-ulds- og møbelfabrikker på 20 mg/m^3 ved 10 % O_2.

Problemstillingen for branchen var i 2002 fortsat ret ny, og der var ikke no-gen kendt teknologi, ud over incinerering, der sikkert kunne fjerne formal-dehyd fra røggassen. Incinerering var og er dyrt på mindre anlæg, hvis der ikke samtidig er en meget høj emission af uforbrændt kulbrinte. Fastholdel-se af kravet ville således reelt betyde et stop for opførelse og udskiftning af nye kraftvarmeanlæg baseret på gasmotorer, indtil alternative løsninger var fundet eller udviklet. Den problemstilling fremlagde branchen for Miljøsty-relsen, og på baggrund heraf udsatte Miljøstyrelsen det i Luftvejledningen fremsatte krav tre år til 1. juli 2006. Udsættelsen blev af Miljøstyrelsen be-tinget af, at branchen igangsatte aktiviteter til afklaring af den bedst tilgæn-gelige teknologi til rensning af gasmotorrøggas for formaldehyd. Dette pro-jektarbejde hviler direkte på dette krav.

Det blev således besluttet af branchen at igangsætte afprøvning af katalysa-torer til reduktion af formaldehyd, og gasnetselskaberne gav tilsagn om at støtte et sådant projekt med miljødokumentation for formaldehyd. Motorle-verandørerne bestilte og opsatte formaldehydkatalysatorer på udvalgte vær-ker, og parallelt hermed skulle formaldehydreduktionen dokumenteres. På

baggrund af DGC's erfaring med emissioner af formaldehyd fra gasmotor-
værker i Danmark blev DGC valgt som projektleder for miljødokumentatio-
nen. DGC foreslog projekt udvidet med yderligere analyser, således at kata-
lysatorernes effekt over for øvrige problematiske emissioner kunne klarlæg-
ges. Eltra (nu Energinet.dk) blev ansøgt og gav tilsagn om støtte hertil under
el-PSO-ordningen.

Der er således i dette projekt gennemført miljødokumentation for feltaf-
prøvning af direkte katalysatorer på tre gasmotoranlæg i Danmark. Herud-
over besluttede GE-Jenbacher tidligt i projektforløbet, at emissionsdata fra
deres egen afprøvning kunne tilgå projektet, således at datagrundlaget blev
udvidet til fire feltafprøvninger.

Det må understreges, at DGC ikke har været involveret hverken i udvælgel-
sen af katalysatorleverandører eller i design og specifikationen af katalysa-
toranlæggene. DGC har ikke kendskab til, hvilke designkriterier motorleve-
randørerne og katalysatorleverandørerne har anvendt.

Katalysatorerne er blevet afprøvet gennem ca. to års normal drift på anlæg-
gene. Katalysatorerne har været fordelt med to katalysatorer fra Süd-Chemie
og to fra Johnson Matthey. Afprøvningen har været gennemført uden større
problemer undervejs. Dog er et anlæg i driftsperioden overgået til det fri
elmarked. Anlægget har på den baggrund haft færre driftstimer end forven-
tet, og den der installerede katalysator opnåede kun 5500 timers drift.

Sammenlignet med den normale driftsperiode for andre katalysatorer på 20-
40.000 timer er testperioden kort. Det er dog med de driftsmønstre, der fo-
rekommer på danske motorer, og med Miljøstyrelsens undtagelse på i alt tre
år ikke praktisk muligt at opnå flere driftstimer.

De opnåede resultater for formaldehyd fremgår af nedenstående Tabel dk1:

Tabel 1   Resultater af formaldehydmålinger gennem hele projektet

	Drifts timer	Formaldehyd		Reduktion	Drifts timer	Formaldehyd		Reduktion
		før	efter			før	efter	
	h	mg/m^3 @ 5% O$_2$, 30 % virkningsgrad		%	h	mg/m^3 @ 5% O$_2$, 30 % virkningsgrad		%
	Jetsmark				Tørring			
Süd Chemie	142	52	22	58	160	34	14	59
	1481	52	26	50	1671	25	13	51
	2402	68	26	61	2947	32	14	55
	4770	54	24	56	4419	34	16	54
	6362	59	28	52	7196	31	14	54
	7129	68	31	55	8228	34	16	51
	8265	58	33	43	10045	33	19	41
	Hjortebjerg				Frederiks			
Johnson Matthey	108	75	3	95	147	49	5	90
	524	103	5	95	2099	49	7	87
	2383	94	10	90	2099	59	8	87
	3514	86	7	92	8831	53	13	75
	4872	109	13	88	10294	73	9	87
	5555	105	15	86	12528	39	6	85

Katalysatorerne fra Johnson Matthey opnåede i starten af driftsperioden omkring 95 % formaldehydreduktion. Efter ca. 10.000 driftstimer er omsætningen dog faldet til omkring 85 %. Katalysatorerne fra Süd-Chemie opnåede omkring 60 % reduktion ved driftsstart, hvilket efter 10.000 timers drift var faldet til 40-45 % reduktion af formaldehyd. På baggrund af resultaterne mener begge fabrikanter, at de kan fremstille katalysatorer, der kan opnå de ønskede reduktionsgrader. Omkostningerne til katalysatormateriale og installation stiger naturligvis med skærpede emissionskrav.

Begge typer af katalysatorer viste gode oxidationsegenskaber over for acetaldehyd, acrolein og CO, ligesom der også blev opnået en lugtemissionsreduktion på omkring 40 %. Katalysatorerne havde kun en begrænset effekt over for kulbrinterne i røggassen. Det var primært for de ikke-mættede kulbrinter som eten, acetylen og propen, der blev observeret en effekt.

Det er et stort aktiv, at katalysatorerne kan løse gasmotorværkernes problemer med acetaldehyd og acrolein.

På de oprindelige tre anlæg i projektet blev der gennemført en detaljeret overvågning af temperaturforholdene omkring katalysatorerne igennem hele perioden. Det blev undersøgt, om katalysatorerne undervejs i afprøvningen blev udsat for ekstreme temperaturer, der kunne medvirke til at ødelægge

deres effekt. Der er med de indsamlede data ikke observeret sådanne meget høje temperaturer.

Dataindsamlingen af temperaturforløbet for katalysatorerne viser meget tydeligt det driftsmønster, som katalysatorerne udsættes for. Danske gasmotorer starter og stopper normalt på daglig basis. Dermed forudsættes, at katalysatorerne kan holde til det termiske stress, som gentagne afkølinger og opvarmninger giver anledning til. Når motorerne stopper deres drift, køres de normalt med lav last en periode for at køle motor og motorolie. I den periode er der set røggastemperaturer, der ligger 60-80 °C over driftstemperaturen ved fuldlast.

Der findes andre metoder til reduktion af formaldehyd. Der er i projektet udgivet særskilt rapport herom /8/. Ved en teknisk og økonomisk sammenligning synes direkte oxidation med katalysator at være det bedste alternativ. Dette er dog følsomt over for primært energipriserne. Med stigende naturgaspris vil metoder, der øger værkernes totalvirkningsgrad ved omsætning af uforbrændt kulbrinte få forbedret driftsøkonomi. Brug af oxidationskatalysatorer force ligger primært i, at investeringsomkostningerne ikke er store, og efter korrekt installation vil omkostningerne og arbejdet med processen være begrænset til udskiftning af katalysatorelementerne, når aktiviteten er blevet for lav.

På baggrund af de indhøstede driftserfaringer er det skønnet, at der ved brug af den dobbelte mængde katalysator i forhold til den i forsøgene brugte mængde på Frederiks KVV vil kunne nås en emissionsgrænseværdi på 20 mg/m^3 @ 5 % O_2 og 30 % virkningsgrad på langt de fleste danske gasmotorværker. En vigtig forudsætning herfor er antagelsen om, at katalysatorerne fortsat langsomt og i samme tempo som hidtil set fra 0 til 10.000 driftstimer taber aktivitet.

På den baggrund ville det være ønskeligt, at der kunne indhøstes erfaringer med katalysatorerne med et større driftstimetal, men dette har ikke været muligt inden for projektets rammer.

4   Introduction and background

Combined heat and power production plays a major role in the energy sup-
ply in Denmark. Combined heat and power production has been financially
favoured in order to obtain large overall energy efficiencies. Gas engines
form an important part of the decentralised combined heat and power plants.
The engine sites accumulate to approximately 450 plants nationwide total-
ling a net production capacity of approximately 900 MW electrical. For a
more complete description of the engines installed on the Danish market,
please see progress report 2 in /1/.

4.1   Emission from gas engines

Emission from lean-burn gas engines in Denmark was well documented in
an emission factor study performed in 2001-2002 /1/. The study showed that
the major emission coming from gas engines consisted of NO_x and un-
burned species ranging from CO through unburned natural gas (unburned
hydrocarbons, UHC) to emissions of partly oxidised or partly burned spe-
cies of ethene, propene and different carbonyl components. The major con-
stituent of the carbonyls is formaldehyde, but also emissions of acetalde-
hyde and acrolein were significant. The study showed that the relative
amount of the small carbonyls (formaldehyde and acetaldehyde) in the ex-
haust compared well to the relative fuel composition of methane and ethane.
Further to these problems some engines sites in Denmark have had prob-
lems and complaints about odour emissions and emissions of lubrication oil
mists.

Since 1998 /2/ the Danish emission regulations for gas engines have in-
cluded emission limits for CO, NO_x and unburned hydrocarbons. The limits
for unburned hydrocarbons were for new natural gas engines only. From
autumn 2006 also engines commissioned before 1998 must adhere to the
limit for unburned hydrocarbons.

4.2   New regulations for formaldehyde

In 2001 the Danish EPA put forward new regulations for formaldehyde
from large engine sites (above 5 MW fired) to be put in force from mid
2003. The emission limit for formaldehyde was 10 mg/m^3 referred to 5 %
O_2, dry exhaust and 30 % electrical efficiency /3/. The engine suppliers in

Denmark complained that the limit was too strict compared to what was possible with the engines themselves and that there was not sufficient data on how to reduce the emission of formaldehyde with exhaust treatment methods.

The proposed Danish emission limit for formaldehyde is seen to be strict compared to the German *TA Luft* (2002) emission limit for gas engines on 60 mg/m^3 @ 5 % O_2. The *TA Luft* value translates to approximately 45 mg/m^3 @ 5 % O_2 and 30 % efficiency for a typical Danish engine with 40 % efficiency.

The US regulation can be seen in US EPA document "*Standards of Performance for Stationary Spark Ignition Internal Combustion Engines and national Emission Standards for Hazardous Air Pollutants for Reciprocating Internal Combustion Engines*" from 2005. The limit is 14 ppm (vol, dry) at 15 % O_2 for 4 stroke engines. This can be recalculated into a limit of 50 mg/m^3 @ 5 % O_2, which will compare to 38 mg/m^3 @ 5 % O_2 and 30 % efficiency for a typical Danish engine with 40 % efficiency.

4.3   Project overview

This project was proposed in order to find possible reductions of formaldehyde at engine sites in Denmark. Based on the project the Danish EPA postponed the formaldehyde regulation for three years.

The project was set up with the following parts:

- Engine suppliers at their own cost set up full-scale tests of formaldehyde reduction catalysts on engine sites in Denmark.

- A literature survey on possible methods for formaldehyde reduction is performed.

- A documentation program is set up to document the possible formaldehyde reduction on the field tests and to document the temperatures at which the catalysts operate during two years of field operation.

- A further documentation program is set up to search for other possible effects of the formaldehyde catalysts. This includes testing for CO, other aldehydes, unburned hydrocarbons and in a few cases odour and lubrication oil mist.

- An expert monitoring group with participants from engine suppliers, Danish EPA, energy companies and other interested organisations is set up to advise and follow the project. See Appendix A.

The literature survey has been reported elsewhere, /8/, and this report focus on the field-test results for formaldehyde and other emissions.

5   Test program

The test program was designed to give useful information to the main question about catalyst capability as a means of formaldehyde reduction and reduction performance in the time scale of thousands of hours of operation on real gas engines in normal operation in Denmark.

The test program further addresses the issue about catalyst performance on other emissions from the engines. This includes emission of other aldehydes, odour, CO, UHC and lubrication oil. The detailed emission performance test collection program is described in Section 5.5.

In order to see if the possible occurrence of critical changes in catalyst performance was to be blamed on changes in catalyst environment, temperature data was collected before and after each catalyst in the project during the field-test period.

DGC has not been involved in the design and specification of the catalyst units. This work has been performed by the engine suppliers and the catalyst suppliers.

5.1   Site Frederiks

Site Frederiks is not part of the actual project, but GE-Jenbacher has kindly decided to share the results from their own test at Fredriks with the other project partners.
The major data for the Frederiks test site is seen in Table 2.

Table 2   Major data for site Frederiks

Type of site	CHP for district heating
Engine make	Jenbacher
Engine type	J 616 GS E11
Engine serial number	3812741
Nominal power	2181 kW electrical
Number of revolutions	1500 rpm
Engine operating hours April 2006	12528 h
Type of catalyst	Oxidation catalyst
Catalyst producer	Johnson Matthey
Catalyst test period in this work	12528 h

5.2   Site Hjortebjerg

Site Hjortebjerg is part of the project. Pon Power has supplied the engine
and the catalyst. The plant is delivering the produced heat to a greenhouse.
During the project period the plant has moved to the liberalised power mar-
ket, causing the plant be operated in fewer hours than expected. Due to this,
the catalyst test at Hjortebjerg accumulated the fewest operating hours for
the catalyst.

Table 3   Major data for test site Hjortebjerg

Type of site	CHP for greenhouse
Engine make	Caterpillar
Engine type	G3520
Engine serial number	GDB 00001
Nominal power	2070 kW electrical
Number of revolutions	1500 rpm
Engine operating hours March 2006	13203 h
Type of catalyst	Oxidation catalyst
Catalyst producer	Johnson Matthey
Catalyst test period in this work	5555 h

5.3   Site Jetsmark

Site Jetsmark is part of the project. GE Jenbacher has supplied the engine
and the catalyst. The plant is delivering the produced heat to a local district
heating network.

The major data for the Jetsmark test engine and catalyst is shown in Table 4.

Table 4   Major data for site Jetsmark

Type of site	CHP for district heating
Engine make	Jenbacher
Engine type	J620 GS E11
Engine serial number	3699771
Nominal power	2801 kW electrical
Number of revolutions	1500 rpm
Engine operating hours March 2006	14140 h
Type of catalyst	Oxidation catalyst
Catalyst producer / supplier	Süd Chemie / Catcon
Catalyst test period in this work	8265 h

5.4   Site Tørring

Site Tørring is part of the project. Rolls Royce has supplied the engine and the catalyst. The plant is delivering the produced heat to a local district heating network.

The major data for the Tørring test engine and catalyst is shown in Table 5.

Table 5   Major data for site Tørring

Type of site	CHP for district heating
Engine make	Rolls Royce Bergen
Engine type	B35:40 V12AG
Engine serial number	17000
Nominal power	5100 kW electrical
Number of revolutions	750 rpm
Engine operating hours February 2006	3168 h (engine have been replaced during project, see text)
Type of catalyst	Oxidation catalyst
Catalyst producer / supplier	Süd Chemie / Catcon
Catalyst test period in this work	10045 h

Due to engine trouble the engine was exchanged at approximately 6.877 operation hours on the catalyst. The new engine was similar to the old one.

5.5 Emission test program

The emission measurements were performed as scheduled in Table 6 to 9 on the different sites. In all cases the measurements were performed before and after the catalyst. Oxygen was measured in all cases in order to be able to correct emission to 5 % O_2.

Table 6   Measuring program at site Jetsmark

Test	Catalyst	Emission component measured							
#	hours	NO_x	CO	UHC	Formaldehyde	Other alde-hydes	UHC specifi-cation	Odour	Lubrication oil
1	142	x	x	x	x	x	x		
2	1481	x	x	x	x	x		x	x
3	2402	x	x	x	x	x			
4	4770	x	x	x	x	x			
5	6362	x	x	x	x	x			
6	7129	x	x	x	x	x			
7	8265	x	x	x	x	x	x	x	x

Table 7   Measuring program at site Tørring

Test	Catalyst	Emission component measured							
#	hours	NO_x	CO	UHC	Formaldehyde	Other alde-hydes	UHC specifi-cation	Odour	Lubrication oil
1	160	x	x	x	x	x	x		
2	1671	x	x	x	x	x		x	
3	2947	x	x	x	x	x			x
4	4419	x	x	x	x	x			
5	7196	x	x	x	x	x			
6	8228	x	x	x	x	x			
7	10045	x	x	x	x	x	x	x	x

Table 8   Measuring program at site Hjortebjerg

Test	Catalyst	Emission component measured							
#	hours	NO$_x$	CO	UHC	Formaldehyde	Other aldehydes	UHC specification	Odour	Lubrication oil
1	108	x	x	x	x	x	x		
2	524	x	x	x	x	x			
3	2383	x	x	x	x	x		x	x
4	3514	x	x	x	x	x			
5	4872	x	x	x	x	x			
6	5555	x	x	x	x	x	x	x	

Table 9   Measuring program at site Frederiks

Test	Catalyst	Emission component measured							
#	hours	NO$_x$	CO	UHC	Formaldehyde	Other aldehydes	UHC specification	Odour	Lubrication oil
	147	x	x	x	x				
	2099	x	x	x	x				
	2099	x	x	x	x	GE Jenbacher data			
	8831	x	x	x	x				
	10294	x	x	x	x				
1	12528	x	x	x	x	x		x	x

All data measured on the engine sites is available in measuring reports for each emission test. For further details about the measuring program and the engine sites please refer to the emission test reports. The data sets for site Frederiks marked "GE Jenbacher data" were limited to the components marked in Table 9. The measuring reports from these tests are the property of GE Jenbacher and the test reports are not available. The GE Jenbacher results from Frederiks are of the same quality as the other results presented in this reports.

5.6   Emission test methods

The emissions were measured with the methods specified by the Danish Ref Lab (National Reference Laboratory on Air Emission Monitoring, www.ref-lab.dk). The Ref Lab has online access to measuring methods for almost all interested components in exhaust from gas engines. The expert monitoring group has had special questions about the formaldehyde test method used in the project. Especially participants from outside Denmark have expressed their interest in the measuring method. For this reason the test method used for aldehydes will be summarised below. The complete Danish text is given in Appendix B

5.6.1   Danish test method for aldehydes

The MEL-12 test method is the Danish EPA recommended method for formaldehyde and other aldehydes. The method is described in detail on Ref Lab (www.ref-lab.dk) in Danish. The method is primarily based on the VDI 3862, blatt 2, 2000 method and the California Air Resource Board method 430 with some modifications. The method uses di-nitro-phenyl-hydrazine (DNPH) as the collecting media. The basic outlay of the method can be seen in Figure 1.
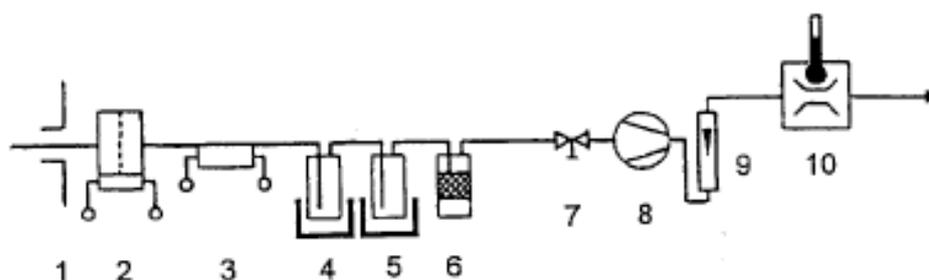
Figure 1   Sampling method for formaldehyde and other aldehydes

The aldehyde sample system is seen in Figure 1. The sample is drawn from the engine exhaust at position 1). 2) is a particle filter that might be used. DGC does not utilise this for gas fired sites. A heated sample line 3) brings the sample gas to the two gas wash bottles 4) and 5), where a solution of DNPH in acetonitril is used as the collection media. DGC always uses a strong solution of 4 g/l DNPH to avoid saturation with aldehydes and to avoid the side reaction with NO_2 to influence the aldehyde sampling /5/.

After the gas washing with DNPH the gas sample is dried 6), pumped and flow adjusted 7-9) and finally metered in a standard gas meter. DGC usually draws a sample of 25-30 litres of exhaust gas from gas engines at a rate of 1-1.5 litres/min.

In a study some years ago /6/, DGC showed that the single wash-bottle efficiency was very high for the small aldehydes. Table 10 summarise the results.

Table 10   Single wash-bottle collection efficiency for four efficiency tests.
The tests were performed in the DGC laboratory using gas engine
exhaust.

Test	Formalde-hyde	Acetaldehyde	Acrolein	Propanal	Butanal	Acetone
1	1.00	0.97	0.95	0.90	0.95	0.88
2	1.00	0.95	0.91	0.83	0.91	0.82
3	0.98	0.86	0.86	0.81	0.86	0.79
4	0.99	0.87	0.75	0.64	0.89	0.79

Due to the high single wash-bottle efficiency DGC in many cases only uses a single wash bottle. In those cases where two bottles were used, the aldehydes were distributed in the wash bottles as expected from Table 10 or better.

After collection the wash bottles were analysed at a laboratory using HPLC.

The exhaust results are calculated from the wash bottle content and the amount of sample gas.

If used properly (which basically comes down to avoiding condensation of water in the sample system) the method has shown very good results in numerous studies, see e.g. /7/. For formaldehyde the measuring accuracy is approximately ± 10 % relative for the emission levels considered in this work. The major problem with the method is that it is rather expensive and time consuming.

6   Emission reduction results

The results of the emission testing are given in the following chapters, where the catalyst effect on different emission components are analysed. All emission data shown in the figures are corrected to 5 % O_2, dry exhaust, unless otherwise is stated.

6.1   Formaldehyde

The main purpose of the project is to see the effect on the emission of formaldehyde using formaldehyde oxidation catalysts. Figure 2 shows the engine emission of formaldehyde before treatment in the catalysts. The figure shows large differences among the engines on the pre-catalyst level of formaldehyde. This will cause the relative demand for catalytic activity to vary significantly among the different engines in order to reach an emission limit. The emissions before the catalyst in this limited study vary from 37 to 143 mg/m^3 at 5 % O_2. Each engine seems to have a certain level of formaldehyde emission, but the actual value varies significantly during time. The reason for the variation is not known specifically, but it is clear that the engine settings have been changed during the test period of two years; see Figure 17 showing variations in engine stoichiometry.
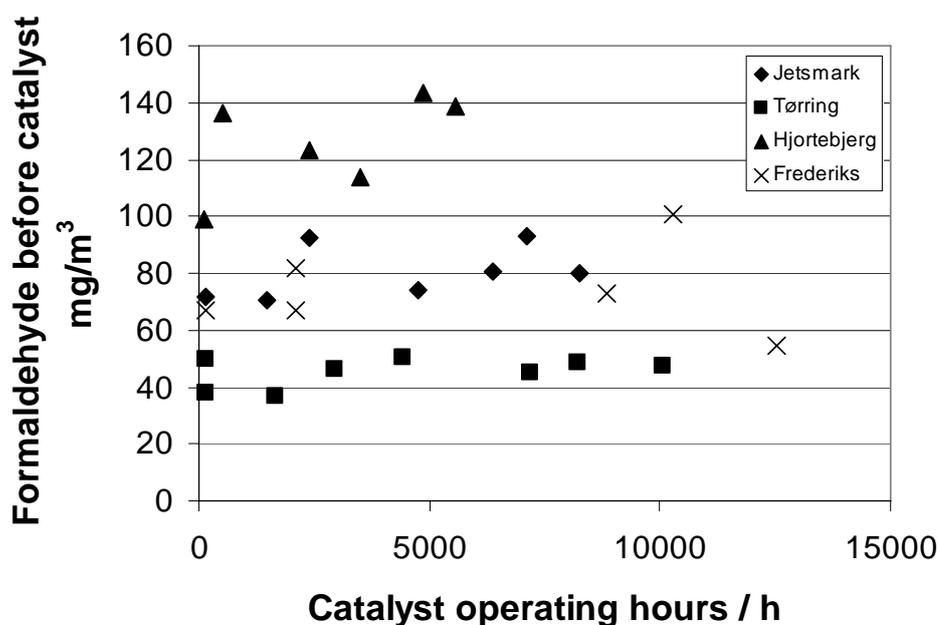
Figure 2   Engine emission of formaldehyde as function of operating hours for the catalysts
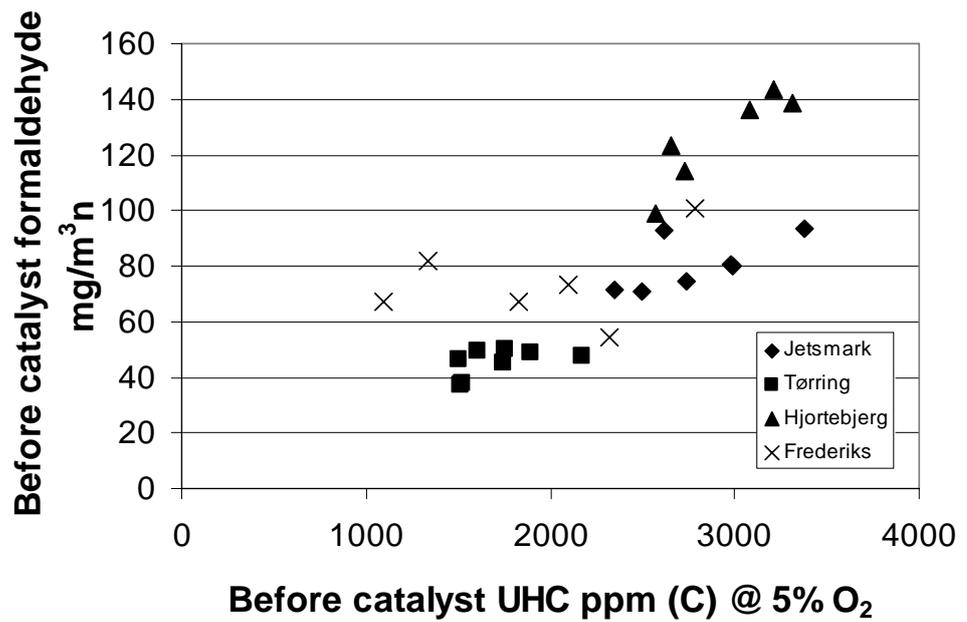
Figure 3   Engine emission of formaldehyde as function of unburned hy-
drocarbons in the exhaust
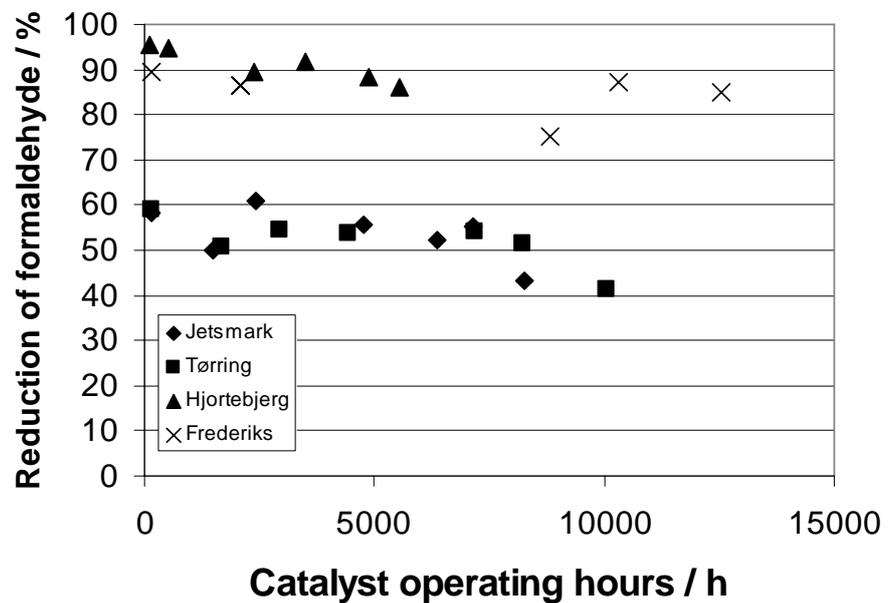
Figure 4   Catalyst reduction of formaldehyde as function of catalyst op-
eration hours

Figure 3 shows the pre-catalyst formaldehyde emission as function of the unburned hydrocarbon emission. Even though the tendency is not very clear for a single engine, the combined data suggests that the formaldehyde emission level is a function of the total emission of unburned hydrocarbons.

Figure 4 shows the formaldehyde emission reduction results from the tested catalyst. The result is given as the formaldehyde reduction as function of the catalyst operation hours. The data is seen to be divided into two groups with each a specific catalyst manufacturer. The Süd-Chemie catalysts (Jetsmark and Tørring) are seen to have formaldehyde reductions starting around 60 % at low operation hours decreasing to around 40-45 % at 10.000 operation hours. The catalyst supplied from Johnson Matthey (Hjortebjerg and Frederiks in Figure 4) have from the start 95-90 % formaldehyde reduction and at Frederiks after 12.500 hours of operation the reduction has decreased to approximately 85 %.

A single test point for Frederiks at approximately 8.800 hours of operation shows a significantly lower reduction, but this was due to a malfunctioning catalyst framework holding the catalytic elements into the correct position. One element was not placed correctly causing some of the exhaust gas to bypass the catalytic elements and thereby causing a lower formaldehyde reduction. When the catalytic element was put back into the correct position the reduction of formaldehyde returned to approximately 85 %.

At Hjortebjerg the catalyst activity has decreased faster than at Frederiks. The Hjortebjerg catalyst activity has decreased to 85 % formaldehyde reduction within 5500 hours of operation.

The large difference in catalyst performance between the two different makes tested cannot be used alone to judge the catalyst ability to reduce the formaldehyde. The difference may alone come from the decided catalyst layout for the Jetsmark and Tørring plant. It will be possible to use the Süd-Chemie catalyst type to obtain higher formaldehyde reduction. This will demand more catalytic activity, which may come from adding more elements of the same catalyst or from a stronger impregnation of the elements with the active components. A stronger impregnation will be preferable if it is possible since just adding more catalytic elements will either cause more

installation costs for a larger cross section or cause a higher pressure loss in the catalyst.

Based on the results both catalyst suppliers have concluded that it will be possible for them to deliver a catalyst with the desired reduction level.

However – it is also clear from Figure 4 that both types of catalyst have a loss of efficiency as the operation hours are accumulated. The losses of activity in the field test performed have been around 10 percentage points in efficiency during the first 10.000 hours of operation (Hjortebjerg in 5500 hours). This will significantly influence the needed catalyst design and the safety margin needed from the suppliers to deliver and warrant certain reduction efficiency during the first years of operation.

6.1.1   Catalyst needed to achieve emission target

Using a rough rule of thumb for designing catalytic treatment plants, it is possible to estimate how much catalyst you need relative to the modules tested in this study. The rule of thumb is that if you double the amount of catalyst, this additional catalyst will work the same way as the first part put in. If the first catalyst section reduced the formaldehyde with, say, 50 %, the additional catalyst will reduce the formaldehyde left over with further 50 %, causing the total efficiency to be approximately 75 %. The costs will be at least double (pressure loss, larger casing, double amount of catalyst).

Figure 5 below shows the obtained formaldehyde reductions with the data from Frederiks and Tørring with the two types of catalyst seen in Figure 4. The observed and extrapolated catalyst performance shown in Figure 5 for the Johnson Matthey catalyst has been used to predict the emission of formaldehyde from gas engines with a high and low emission level using one or two modules of catalyst. The high emission level corresponds to the formaldehyde emission at the Hjortebjerg plant and the low emission to the level at the Tørring plant, 110 and 35 mg/m^3 @ 5% O_2 and 30 % efficiency, respectively. The emission levels from these two plants represent the spread on formaldehyde emissions observed among Danish gas engines very well /1/. The results can be seen in Figure 6.
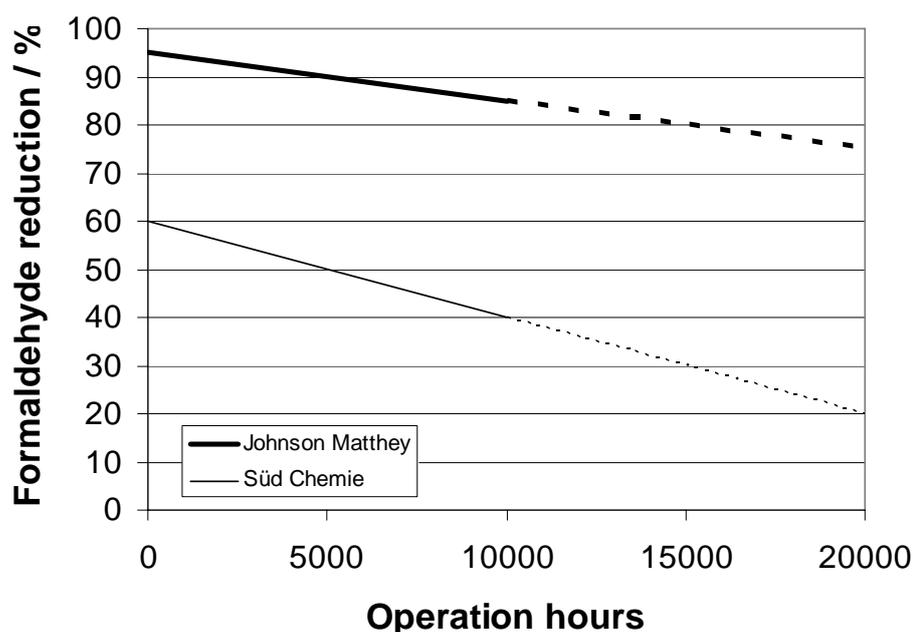
*Figure 5   Catalyst reduction of formaldehyde. Dashed lines are extrapola-
             tions for additional hours of operation.*

Figure 6 reveals that one catalyst module will only solve the problem and
lower the formaldehyde emission sufficiently to reach the Danish EPA
emission target of 10 mg/m^3 @ 5% O_2 and 30 % efficiency for 4500 hours
of operation if the engine has a high pre-catalyst emission of formaldehyde.
Using the double amount of catalyst will solve the problem for above
20.000 hours of operation. An engine with a low emission level is predicted
to reach the target with one catalyst module for more that 20.000 hours of
operation.

Using the same extrapolation and rule-of-thumb calculation as above, the
needed number of Johnson Matthey, Figure 7, and Süd Chemie, Figure 8,
can be estimated. In Figure 7 an extrapolation to 40.000 hours of operation
has been performed. This clearly increases the uncertainty on the predicted
catalyst demand considering the test length of a little above 10.000 hours,
however, the extrapolation is the best possible with the available data.

From Figure 7 it is estimated that using two modules of Johnson Matthey
catalyst comparable to the one used in the Frederiks plant will reach an
emission target of 20 mg/m^3 @ 5% O_2 and 30 % efficiency for most Danish
gas engines within a 40.000 hours operation time span.
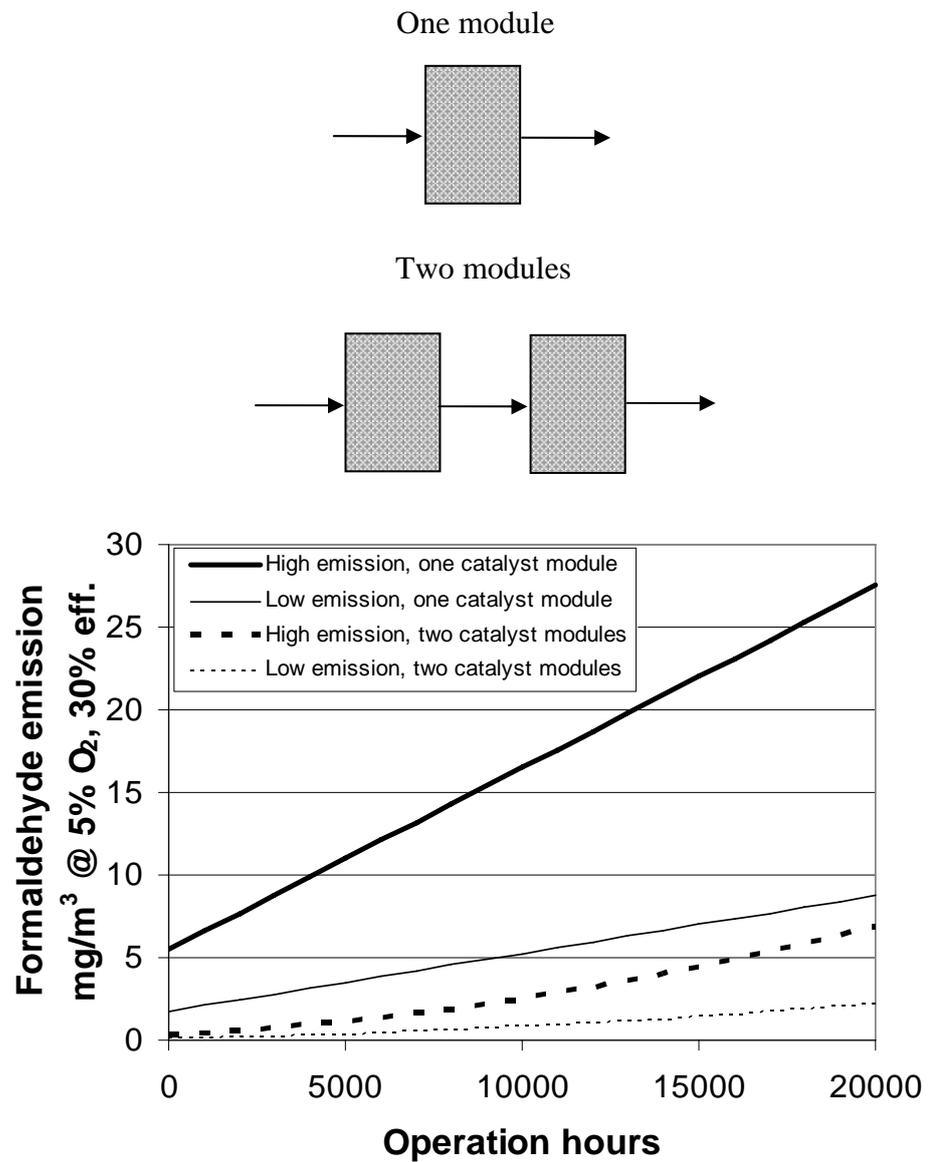
One module

Two modules

Figure 6   Predicted formaldehyde emission using one and two modules of catalyst. See text for detailed explanation.

Using the catalyst from Süd Chemie will demand a high number of catalyst modules comparable to the one module used at the Tørring plant. This might cause problems with a too high pressure drop or too large room needed for the installation.
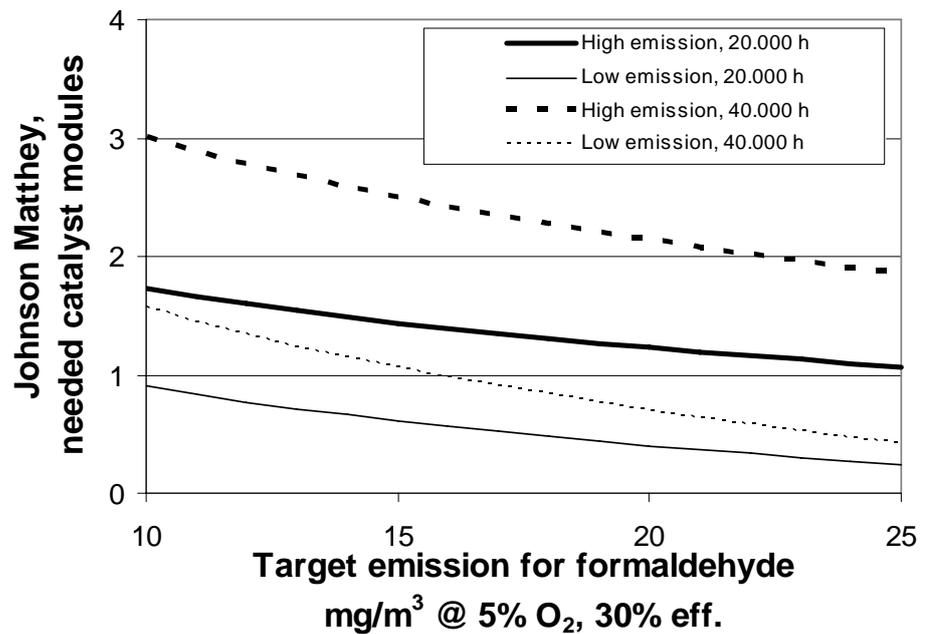
*Figure 7   Predicted Johnson Matthey catalyst demand for specific emis-
              sion target. Note that catalyst performance has been extrapo-
              lated from 10.000 hours of operation. This causes uncertainty
              on the predicted amount of catalyst.*
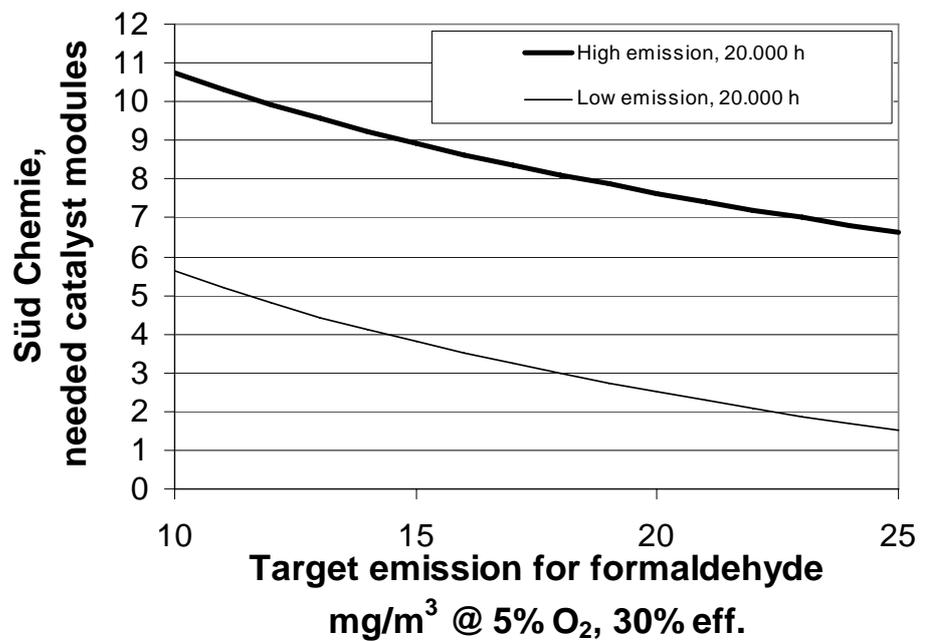
*Figure 8   As Figure 7, but for Süd Chemie catalyst. It is not possible to
              extrapolate to 40.000 hour for this catalyst.*

6.2   Other aldehydes

The emission of formaldehyde is not the only emission of carbonyl species from the gas engines. Other carbonyl compounds are also present in the exhaust, but in lower levels. DGC have previously documented that up to C_6-carbonyls are present in the exhaust gas /1/. In this work we focus on acetaldehyde and acrolein. Acetaldehyde is the second most common aldehyde in gas engine exhaust. As for formaldehyde it is formed by partial oxidation of the natural gas. Figure 9 shows the emission of acetaldehyde as function of the emission of unburned hydrocarbons. The functionality is not seen as clear as for formaldehyde. The emission of acetaldehyde is in line with previously collected data in /1/ and the emission is typically 3 to 10 mg/m^3. In /1/ a very clear correlation between the amount of formaldehyde and acetaldehyde was found. The acetaldehyde is expected to follow the C_1/C_2 ratio line for the fuel shown in Figure 10 on the lower side of the line. This is indeed true for the data from Tørring, Jetsmark and Frederiks, but the data from the Caterpillar engine in Hjortebjerg differs from this pattern. The lower amount of acetaldehyde is somewhat puzzling. The reason for the lower acetaldehyde than expected might be a catalytic effect in the exhaust system or a high temperature environment in the exhaust channels after the cylinder oxidizing some of the acetaldehyde. The amount of acrolein emission from the Hjortebjerg engine is not an outlier compared to the other engines, see Figure 11, while the propanal emission shown in Figure 12 again shows significantly lower emissions from the Hjortebjerg engine than what should be expected from the emission of unburned hydrocarbons.

Figure 13 shows the catalyst effect on acetaldehyde. The reduction of acetaldehyde is almost showing the same picture as for formaldehyde. The catalysts also show some loss of efficiency as the operation hours are accumulated. For the C_3-carbonyls (acrolein, propanal and acetone) the catalyst shows the same behaviour, but the data starts getting more scattered due to the influence of uncertainty on the ratio of two small figures.
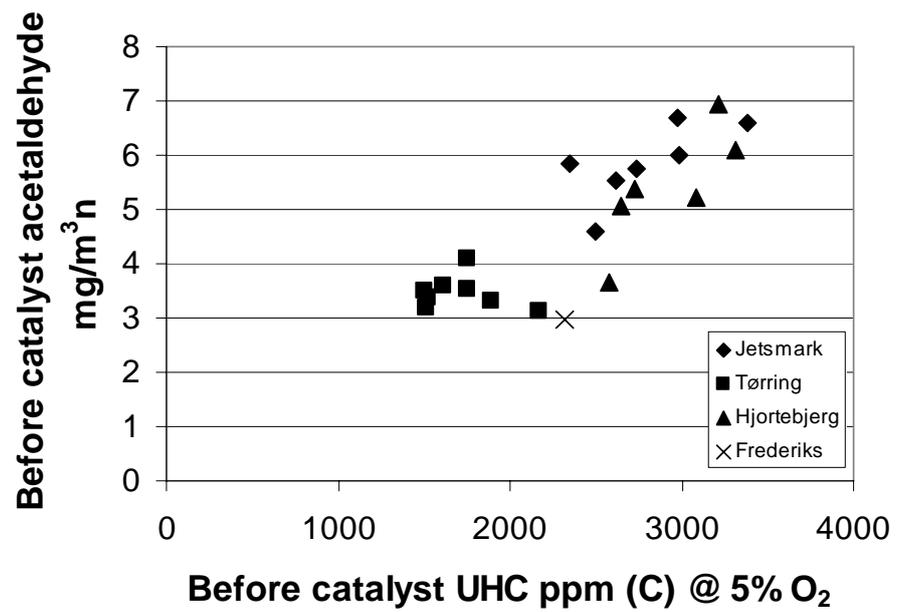
*Figure 9   Engine emission of acetaldehyde as function of the emission
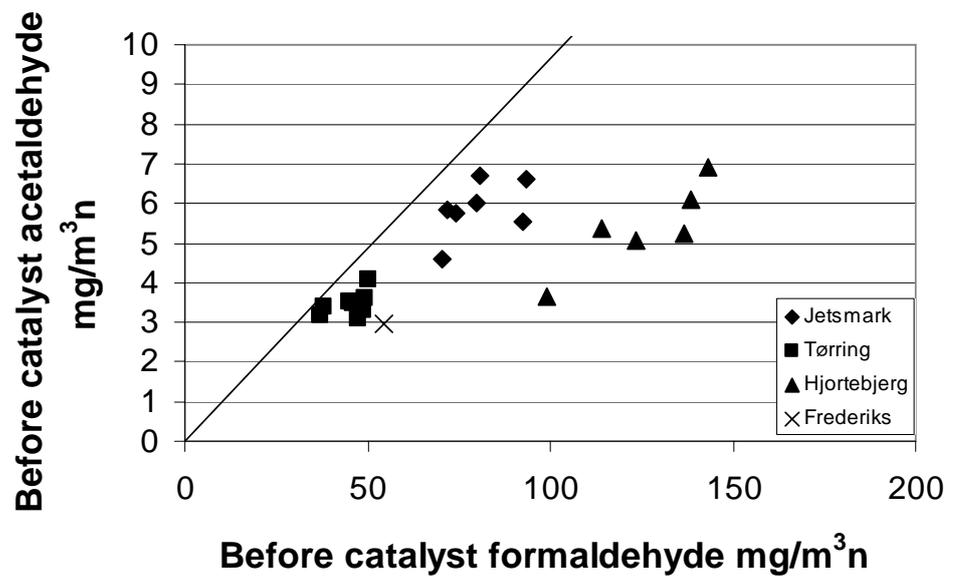   level of unburned hydrocarbons*

*Figure 10   Engine emission of acetaldehyde as function of the emission
             level of formaldehyde. The line represents the ration among
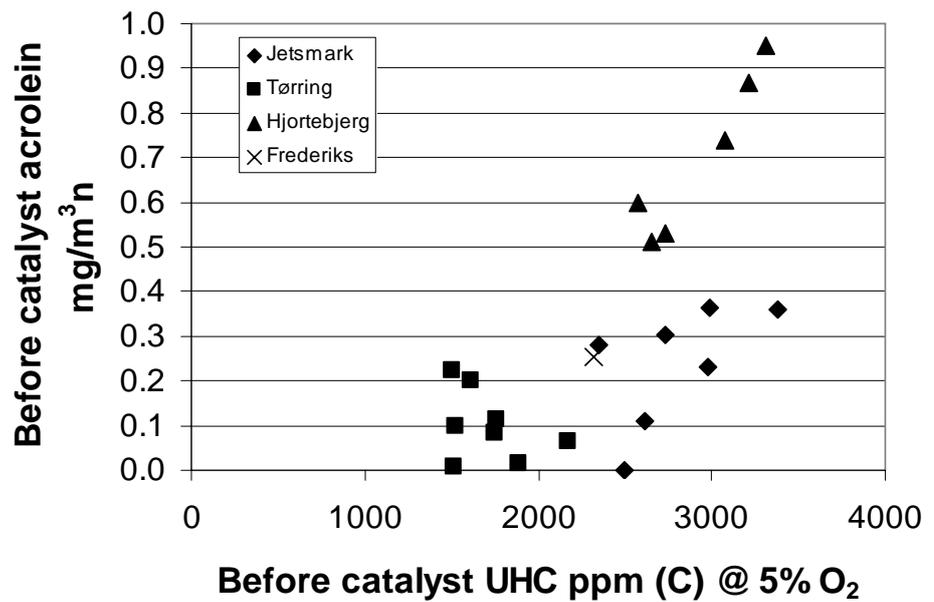   methane and ethane in the natural gas fuel.*

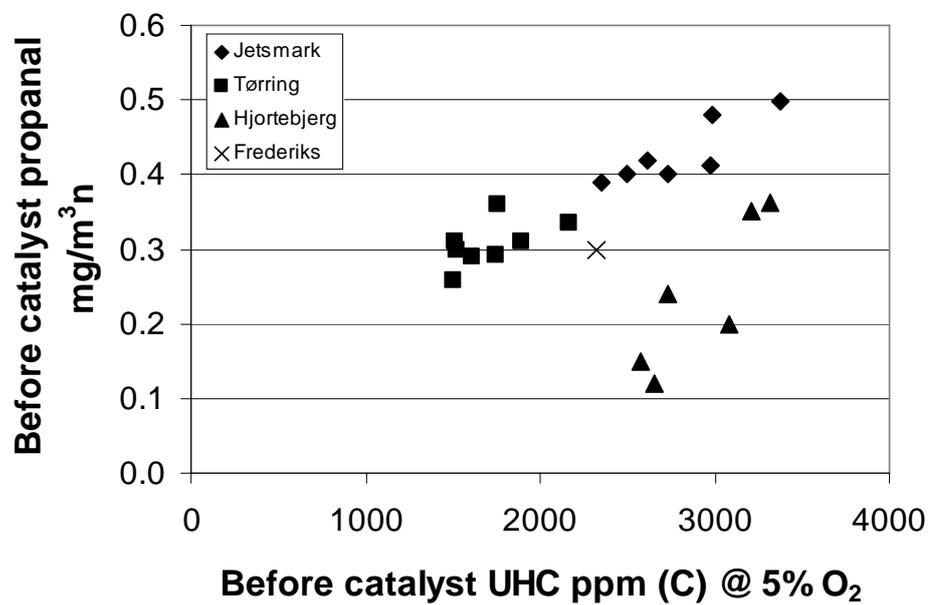*Figure 11   Engine emission of acrolein as function of the emission level of
unburned hydrocarbons*

*Figure 12   Engine emission of propanal as function of the emission level of
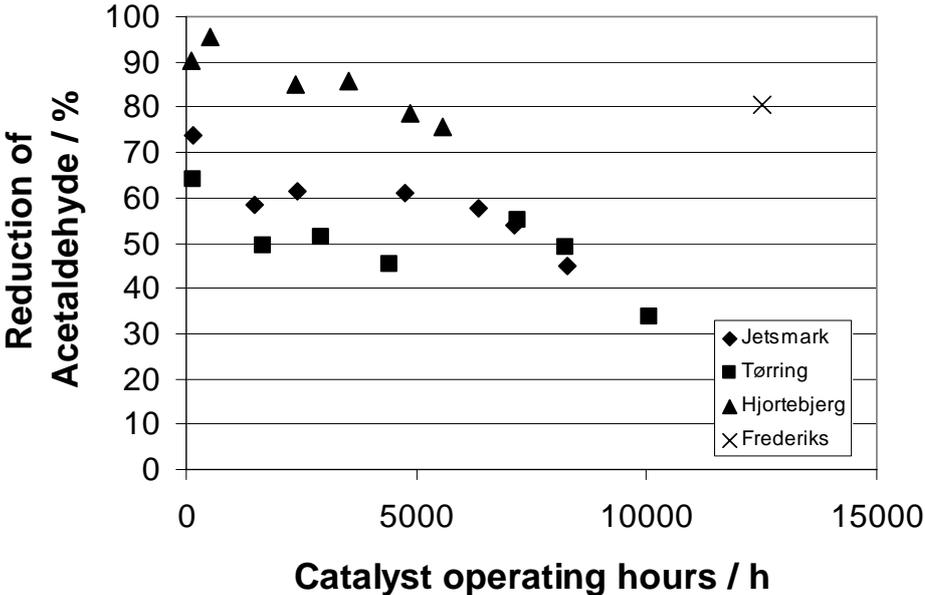unburned hydrocarbons*

Figure 13   Catalyst reduction of acetaldehyde as function of operation
hours

6.3   UHC

The catalyst used in the field test was not expected to have a significant re-
duction effect on the emission of unburned hydrocarbons. Figure 14 shows
that the effect is indeed not very large. The Süd-Chemie catalyst shows a
stable reduction of approximately 4 to 6 % of the emission of unburned hy-
drocarbons. The Johnson Matthey catalyst showed a reduction of unburned
hydrocarbons of 15 % at Hjortebjerg at low numbers of operation hours.
The Frederiks data was non-conclusive at the low number of operation
hours, but it seems likely that the Johnson Matthey catalyst ends around 6 %
reduction of the unburned hydrocarbons at 10.000 hours of operation.

A few emissions were analysed using a gas chromatograph to further spec-
ify the effect on unburned species. It is clear from this analysis that the Süd-
Chemie catalyst does not oxidise ethane or propane, while the Johnson Mat-
they has a small oxidising effect on these components. Both catalysts to a
large degree oxidise the unsaturated components present, see Figure 15 for
the ethene data. A minor oxidising effect was seen for the C_4+ hydrocar-
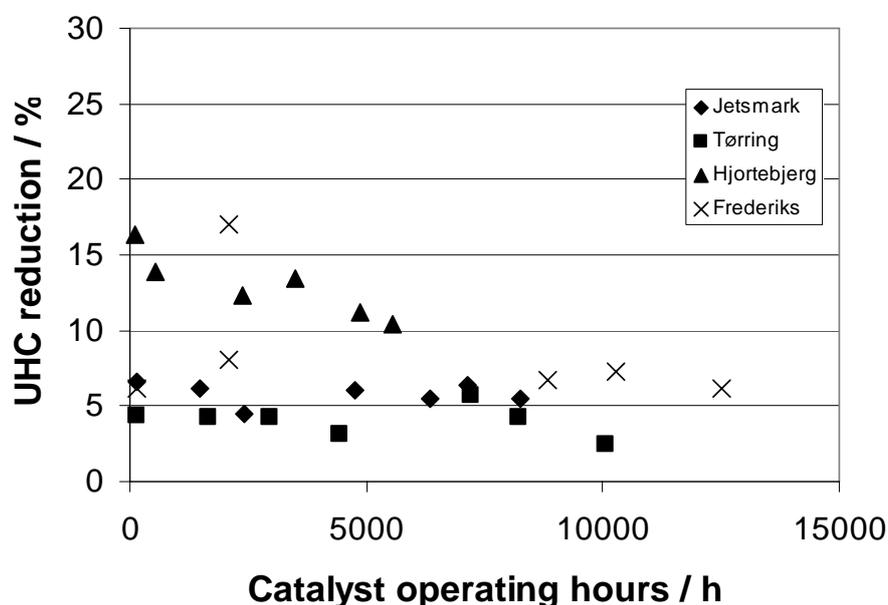bons.

Figure 14   Catalyst reduction of unburned hydrocarbons as function of
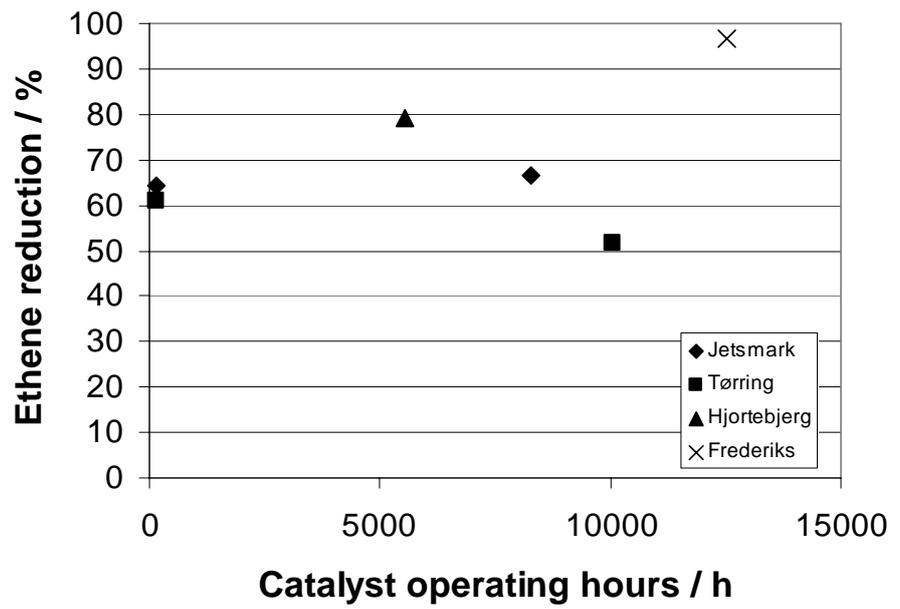*operation hours*

Figure 15   Catalyst reduction of ethene as function of operation hours
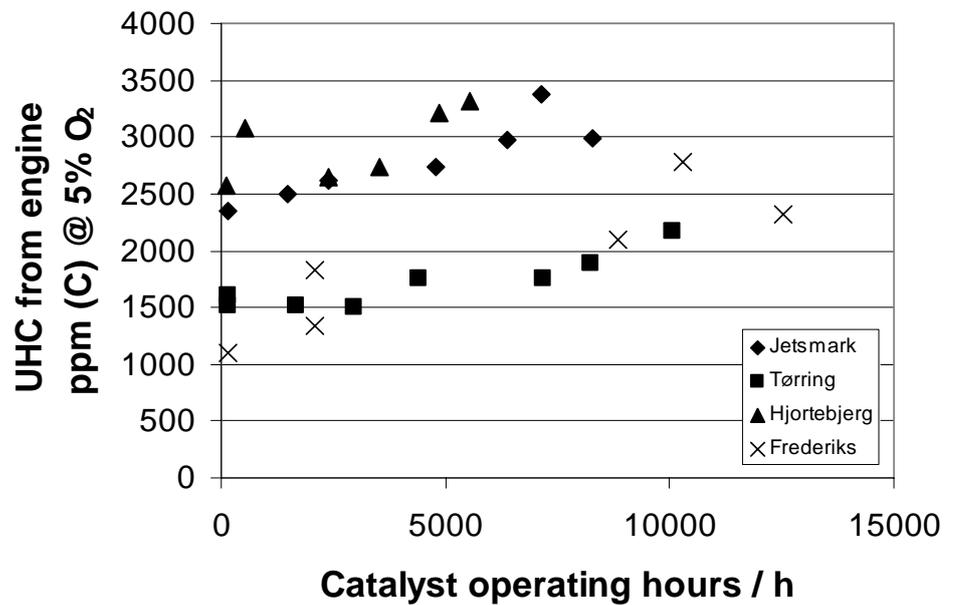

*Figure 16   Stability of UHC emission from the engines as function of op-
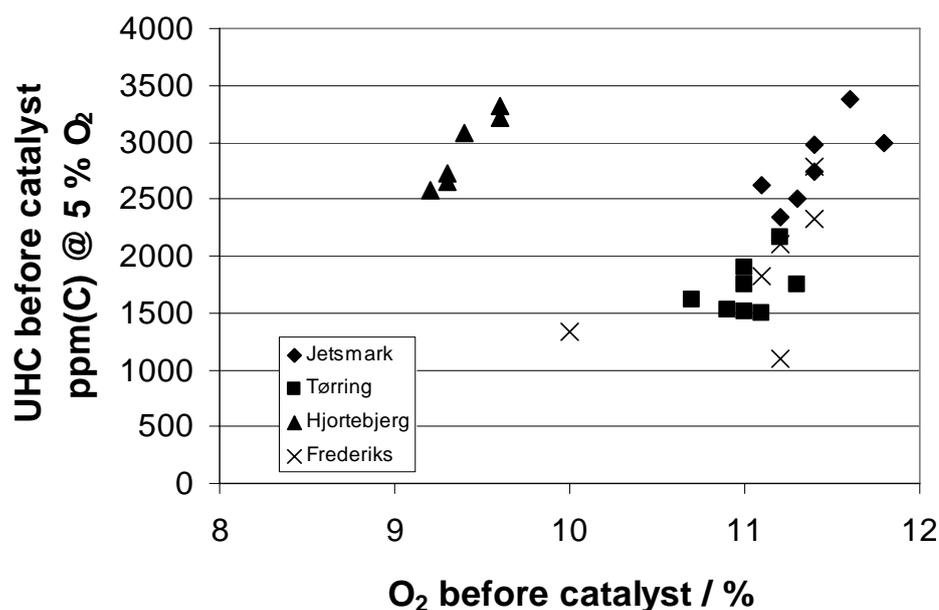eration hours*

*Figure 17   Stability of UHC emission from the engines as function of en-
               gine stoichiometry*

In the emission factor study /1/ very stable emissions of unburned hydrocar-
bons were seen in the annual emission performance measurements for indi-
vidual engines. Several of the tested engines showed stable emission for the
several years investigated. Contrary to this understanding of the emission,
all the engines in this study showed increasing emission of unburned hydro-
carbons throughout the study period. This topic, therefore, needs to be ad-
dressed further in a coming emission factor study. As can be seen in Figure
16, a significant increase in emission of unburned hydrocarbons was ob-
served for all four engines during this project time span of two years of op-
eration. All engines show an increasing emission of approximately 500 ppm
(C) for 10.000 hours of operation. The reason for this trend might be seen in
Figure 17. It is clear that the engine settings for the plants have been
changed during the project time span. It is not clear for which reason the
engine stoichiometry has been changed, but one reason might be the wish to
reduce the NO_x emissions. Another thing that might influence the data is
that the engines in this case are all quite new. The initial wear on the engines
will probably increase the UHC emission. Nevertheless, emissions of un-
burned hydrocarbons were less stable than expected from the previous
study. The Danish gas quality has been very stable in the test period, and
gas variations cannot be responsible for the observed differences.

6.4   CO

CO is normally one of the easiest components to oxidize catalytically. Both types of catalyst tested in this field study showed good oxidation capability towards CO. Figure 18 show the CO oxidation during the field test. CO oxidation for the Süd-Chemie catalyst has been around 90 % in Tørring and around 97 % in Jetsmark. The Johnson Matthey catalyst showed very good CO oxidation capabilities in Hjortebjerg, around 98 % and in Frederiks the catalyst had around 97 % of CO oxidation with the exemption of the one measurement performed when the catalyst element was displaced allowing exhaust gas to bypass the catalyst (see Figure 4 and Section 6.1).

The engine CO level showed some instability during the two-year time span of the test period. The variations can be seen in Figure 19. The major cause for this is again thought to be changes in stoichiometric ration, engine adjustments (ignition timing) and wear. Figure 20 shows the engine CO level as function of stoichiometry. The CO oxidation capability of the catalyst for formaldehyde is an additional benefit, since almost all engines today need a CO catalyst in order to be within the CO emission limits. If a formaldehyde catalyst is to be used, the plant owner will no longer need the CO catalyst. The formaldehyde catalyst will cause CO emission levels to be significantly lower than emissions limitations.
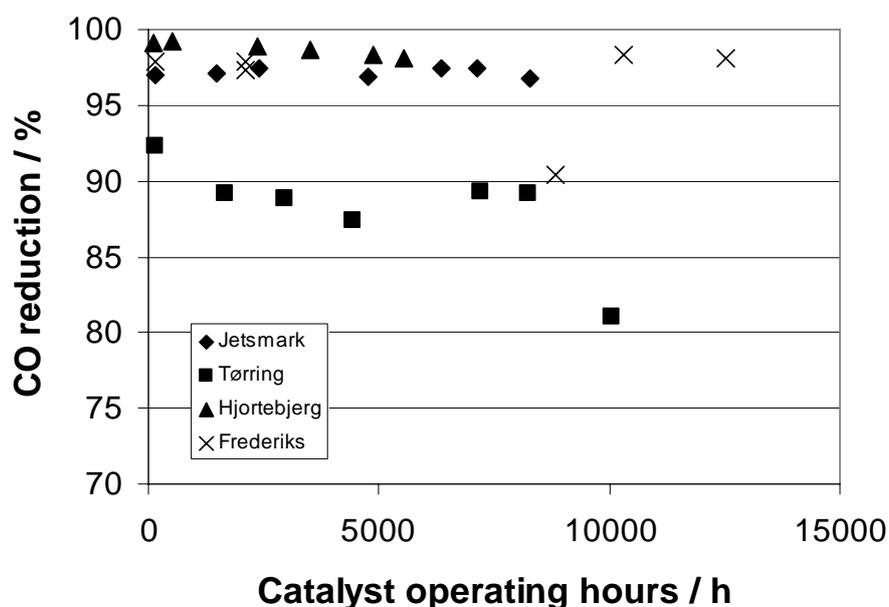

Figure 18   CO emission reduction during field test of catalyst

Figure 19   CO emission before catalyst during field test of catalyst

Figure 20   CO emission before catalyst during field test of catalyst

6.5   Odour

Some years ago, around 1996 to 1998, several Danish engine sites received
many complaints about odour. The main problem was that neither the plant
owners nor the advisors at that time were attentive to the odour emission
from the engines. The stack design was done traditionally as for boilers,
with NO_x as the designing parameter. This caused some of the stacks to be
too low giving odour problems for neighbours to some plants. The problems
have now been solved by building higher stacks, and today advisors design-
ing new plants know that they need to pay attention to the odour emission.
Furthermore, the Danish EPA has imposed new regulations for odour emis-
sion from new gas engines.

The field test of the formaldehyde catalyst was expanded with odour meas-
urements to see if the catalyst has an effect on odour emission. The results
obtained for odour reduction can be seen in Figure 21. As can be realised
from the figure, the odour reduction was not very stable. Odour measure-
ments are made by presenting diluted samples of exhaust to a human panel.
The results are of log scale type causing the uncertainty to be approximately
a factor of two. This, of course, influences the broad picture when looking
for odour reductions, and often causes the results to be scattered. The engine
emission of odour during the test period can be seen in Figure 22. Please
note that data are not corrected to 5 % O_2. Due to the uncertainty level the
sampling and tests were always performed as double measurements. The
odour emission measurements showed good reproducibility during the tests
performed here, and the emission was in the range from 4.000 to 14.000
odour units. This is in range with a larger study showing average emission
around 8.000 odour units from Danish natural gas engines /1/.

In order to clarify the catalyst effect on odour emissions a statistical test was
performed on the reduction data seen in Figure 21. The statistical test was
performed both assuming that the odour data follows a normal distribution
or a logarithmic normal distribution. The results can be seen in Table 11.

Table 11   Statistical analysis results for the odour reduction data. The table
shows at which degree of certainty (significance level) we can
conclude that the catalyst has an odour reduction effect.

Type of catalyst	Normal distribution	Log normal distribution
Both types	99.9 %	99.95 %
Süd-Chemie	99.5 %	99.95 %
Johnson Matthey	97.0 %	99.5 %

From the results shown in Table 11 it is very certain that the catalyst has an
odour reducing effect, both seen as a united group and divided into the two
types of catalyst. The reduction effect for the Süd-Chemie catalyst was
based on an average from 9300 before the catalyst to 5100 odour units after
the catalyst. The similar results for the Johnson Matthey catalyst was from
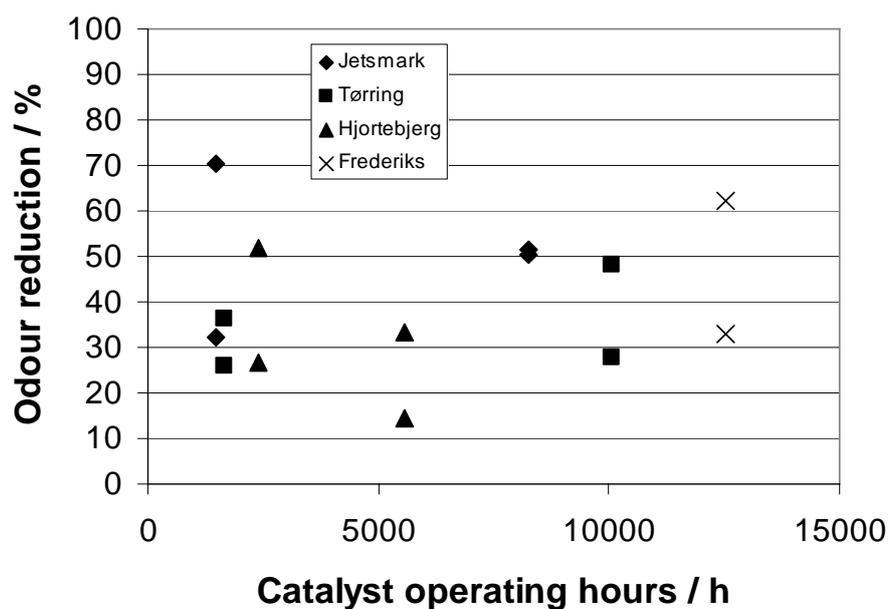7400 before the catalyst to 4400 odour units after the catalyst.

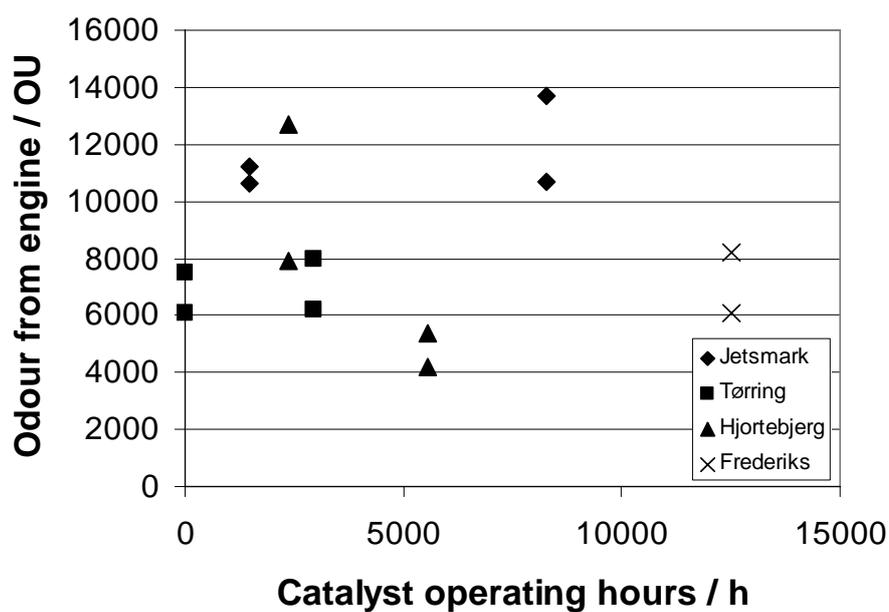*Figure 21   Odour emission reduction during field test of catalyst*

*Figure 22   Odour emission before catalyst during field test of catalyst, data
are not corrected to 5 % O_2*

6.6   Lubrication oil

The emission mapping study /1/ showed that natural gas engines have a sig-
nificant emission of lubrication oil, either as gas phase oil vapour or as oil
mists (aerosols). The measuring program included a few oil emission meas-
urements, but due to very unfavourable sampling conditions on the field-test
sites the results were non-conclusive. Details about the oil sampling results
can be seen in the emission test reports.

7 Results from temperature data collection

During the field test of the catalyst, exhaust temperatures before and after the catalysts were collected. The main idea was that it might prove useful for the catalyst producers to see the temperature environment in detail, in which their catalysts are expected to operate. In previous studies of direct catalysts tested for unburned hydrocarbon oxidation capabilities there has been speculation about the reason for the loss of efficiency observed. The speculation has focused on the catalyst sometimes experiencing much higher temperatures than expected. The high temperature could come directly from the exhaust gas or by the catalyst oxidizing high amounts of hydrocarbons. It was, therefore, decided in this project to collect exhaust temperatures before and after the catalyst.

A temperature acquisition system was placed at each site (Tørring, Jetsmark and Hjortebjerg) originally in this study. At site Frederiks where GE Jenbacher kindly has provided emission data to the project no temperatures were acquired.

In order to see short-time temperature effects, temperatures were collected once each second during the two years of field testing. This is a large quantity of data, and the data has not been studied in detail. DGC will be pleased to provide the data to any interested party, and catalyst producers are invited to request the data for their own installation for detailed analysis. The following Figures 23 to 37 give examples of the data, and the results will be commented briefly in the following text.

After the field test, data also proved to be interesting from another point of view. At site Hjortebjerg a change in plant operation strategy has occurred during the field-test period. Hjortebjerg has changed to the liberalised market for power causing a larger number of starts and stops and fewer operation hours. This can be studied in detail using the temperature data, and the shift in strategy will also influence the catalyst operation environment.

7.1 Engine operation pattern

Figures 23-27 show the maximum exhaust gas temperature observed during the last hour of operation. In order to get a brief overview of the temperature data they were processed for hourly maximum, minimum and average values. None of the sites were exposed to extremely high temperatures during the field test period, and the results presented here are very typical for the test sites.

For many years, engines in Denmark have operated in a specific pattern with the layout defined by the specific price setting for the power produced. This pattern can be seen clearly in Figures 23, 25 and 26. The engine sites are trying to maximise production during daytime Monday to Friday, where power prices are or used to be high and to stop engines during the night and weekends. As can be seen for site Tørring in Figure 26 the plant was in operation also in weekends. The operation pattern will change during the seasons due to the change in heat demand from the site. This is also seen in Figure 27 representing late November to December conditions. At this time of the year the plants will operate more continuously in order to produce the needed heat for the district heating costumers. On the contrary, in the summertime engine sites may usually operate only a limited number of hours each day.

Figure 24 shows the effect of changing to the liberalised power market. Site Hjortebjerg has compared to Figure 23 changed operation strategy causing a larger number of starts and stops and fewer operation hours.

It is expected that a large fraction of the engine sites in the future will move to the liberalised power market. This will cause conditions for catalysts to change, increasing the number of starts and stops. The change might influence the catalyst loss of efficiency and durability due to more thermal fluctuations putting more stress on the materials.
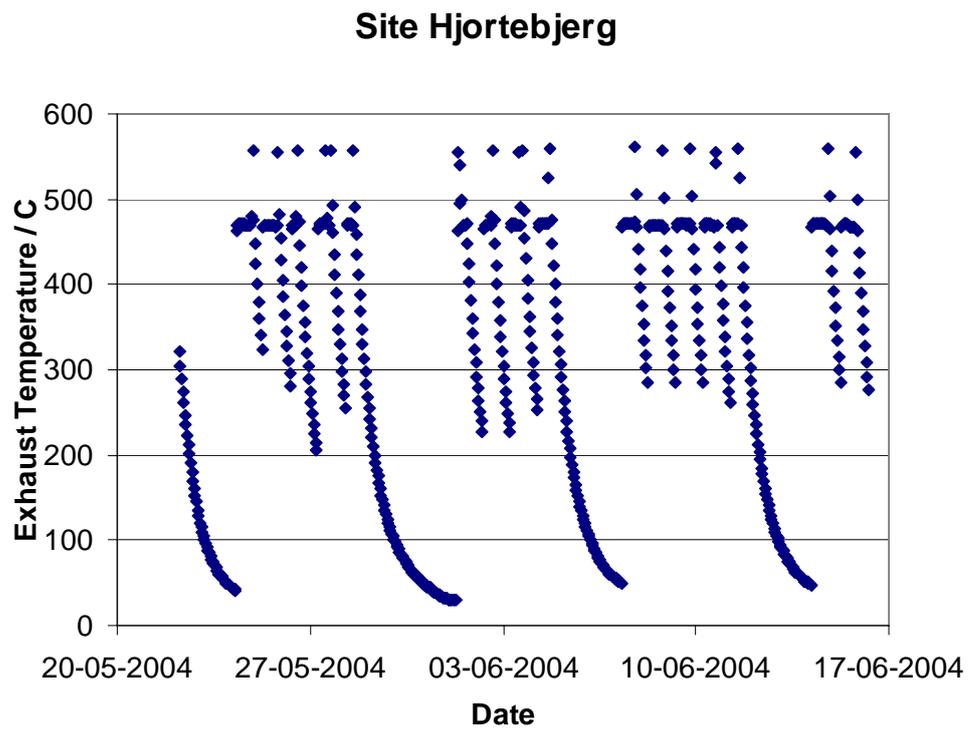
Site Hjortebjerg

Figure 23   Temperature before catalyst during field test of catalyst

Site Hjortebjerg

Figure 24   Temperature before catalyst during field test of catalyst

Site Jetsmark

Figure 25   Temperature before catalyst during field test of catalyst
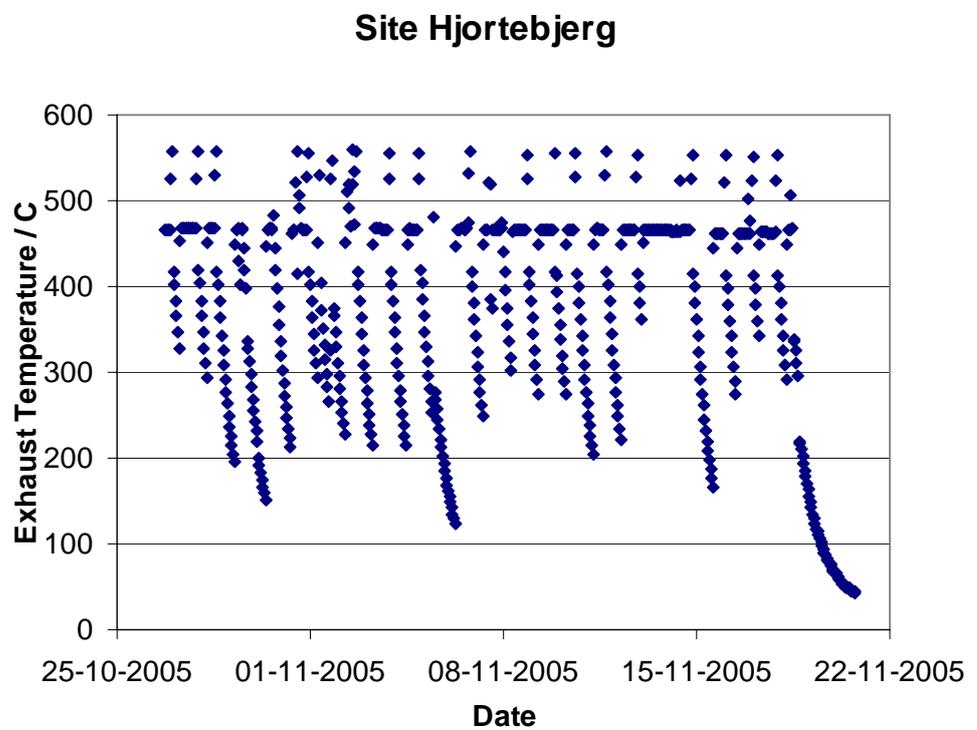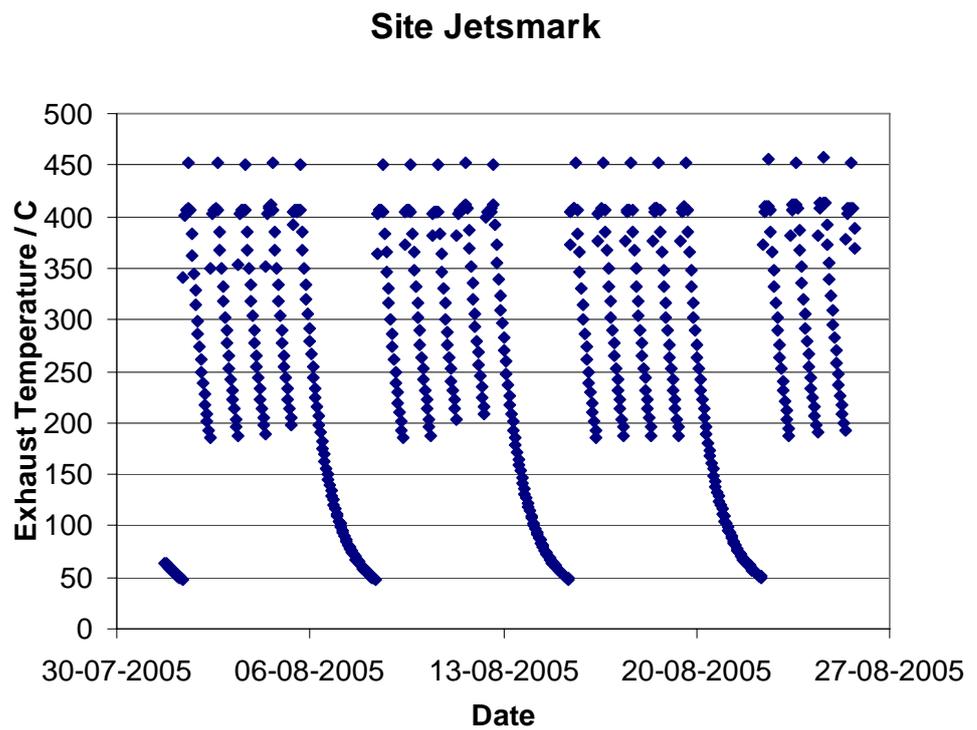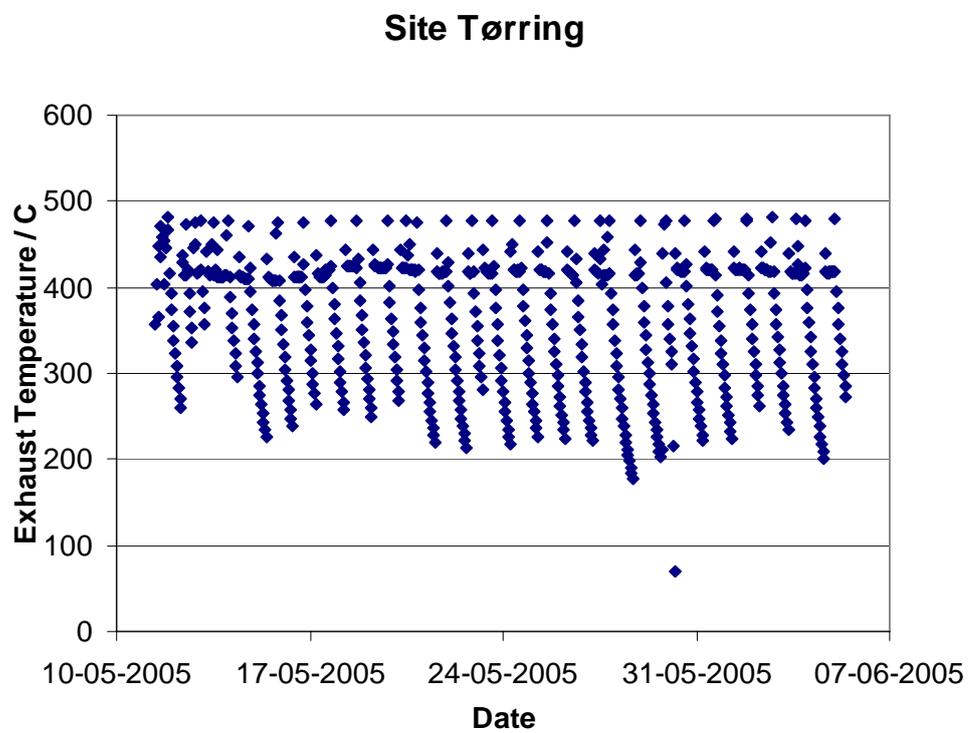
Site Tørring

Figure 26   Temperature before catalyst during field test of catalyst
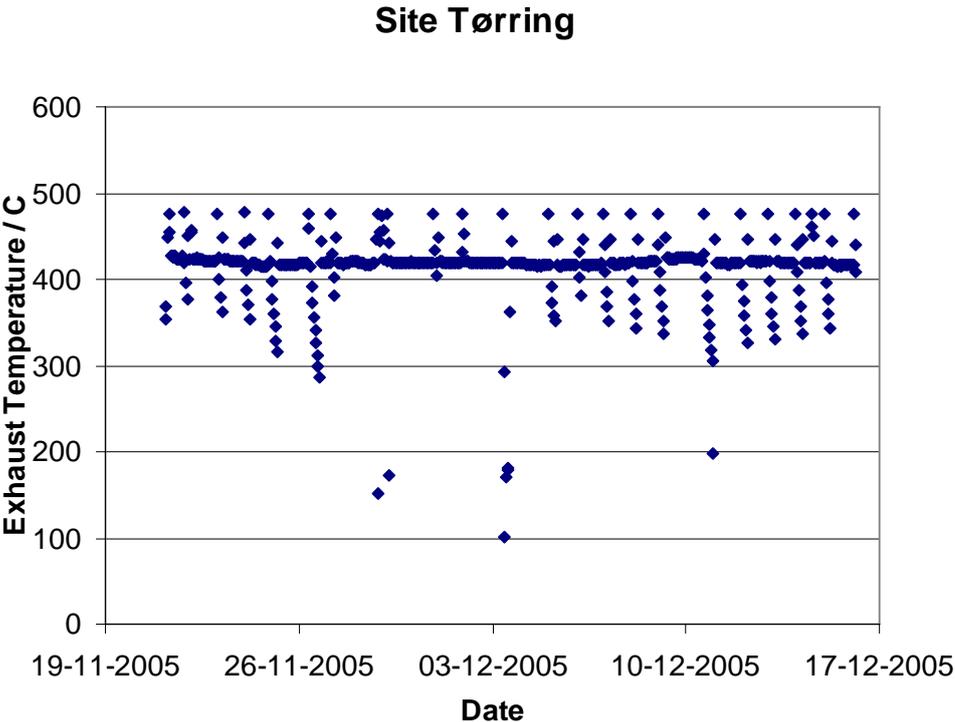
Site Tørring

Figure 27   Temperature before catalyst during field test of catalyst

7.2   Short-term temperature variations for catalyst

The temperature changes during start, stop, normal operation, air flushing, and emergency stop have been analysed further using some of the detailed data obtained. Also, exhaust temperature data from an engine breakdown was obtained.

Figure 28 shows the exhaust temperature before and after the catalyst at site Tørring during start up in the morning. At 6.00 the engine system starts to flush the exhaust system with air causing the temperature to decrease sharply. At 6.10 the engine starts and after approximately 20 minutes of operation the exhaust temperature becomes stable around 420 °C. After further 15 minutes of stable operation at 6.45, the engine is emergency stopped. The temperature profile of the emergency stop is different from the normal stop temperature profile seen in Figure 29. At the emergency stop, the engine is stopped immediately for safety reasons and the exhaust temperature decreases immediately. At the normal stop, the engine is de-rated to cool down the engine and the engine oil before stopping the engine. At the Tørring site this causes the exhaust temperature to increase by 40 to 60 °C during the 15 minutes engine cooling period. After the stop at 6.45 the engine operator system tries to start the engine at 6.52, but for some reason the start is not successful. At 7.05 the engine is started successfully and after 15 minutes the exhaust gas temperatures becomes stable.

Figure 29 shows a normal stop with the above described temperature increase during the engine cool down period. When the engine is finally stopped, the exhaust temperature decreases dramatically due to the air flushing. Air flushing is used for safety reasons. It is known that during start and stop periods the engine exhaust contains large amounts of unburned natural gas. In order to avoid exhaust system explosions, flushing with air is performed. The different engine sites may follow different air flushing strategies such as before start, after stop, and/or both. Due to the flushing the catalyst will experience steep exhaust gas temperatures. Figure 30 shows the stable exhaust temperatures during normal operation. Engines in Denmark typically have exhaust temperatures from 400 to 450 °C.

An ongoing PSO project is focusing on the start/stop emissions from gas engines. Further information on this project can be obtained at DGC.

Site Tørring double start
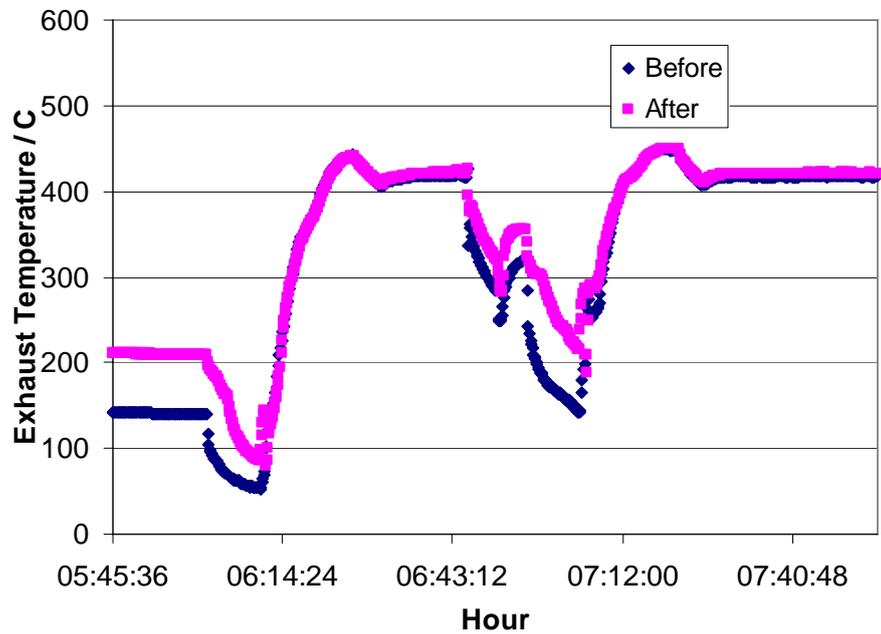
*Figure 28   Temperature before and after catalyst during engine start up.
Two successful starts and one failed start can be seen*

Site Tørring stop
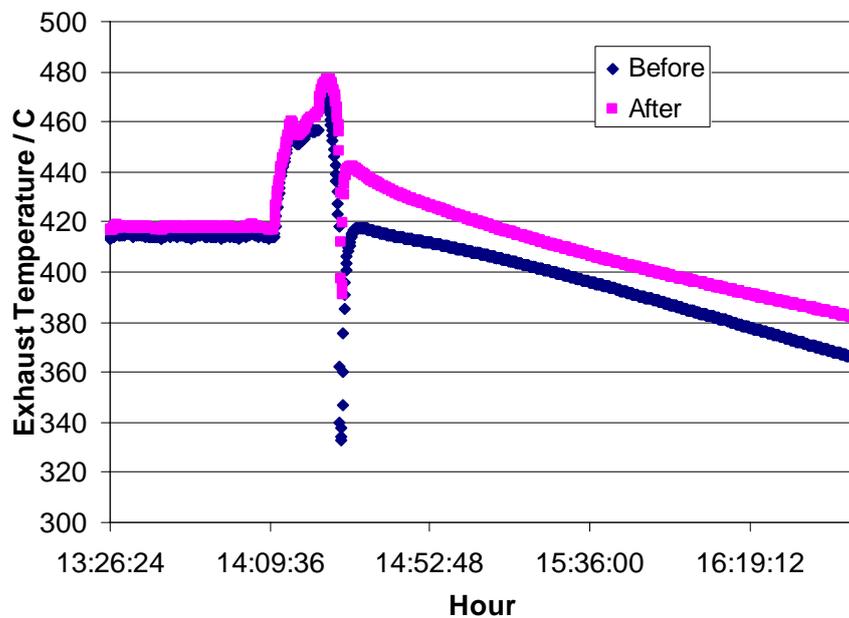
*Figure 29   Temperature before and after catalyst during normal engine
stop. Sharp temperature decrease after stop is due to air flush-
ing.*

Site Tørring stable operation
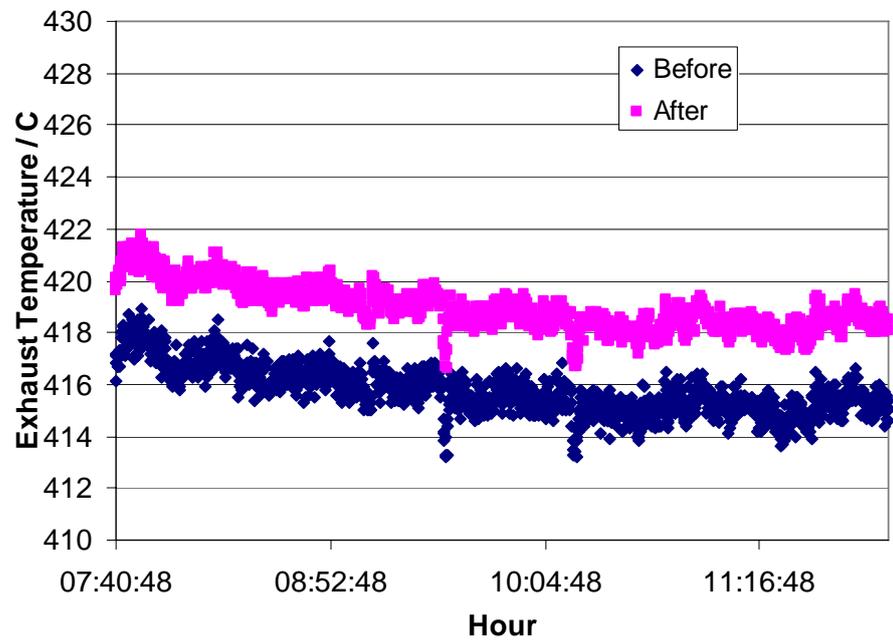
Figure 30   Temperature before and after catalyst during stable operation

Site Hjortebjerg start

Figure 31   Temperature before and after catalyst during engine start

The temperature profile during engine start at site Hjortebjerg has the same basic features as does the start at site Tørring. Figure 31 shows the temperature during start of the Hjortebjerg engine. At 7.30 the engine starts. After approximately 15 minutes the exhaust gas temperatures before and after the catalyst have almost reached their final stable levels.

During engine stop at Hjortebjerg we observed the same temperature rise as in Tørring, see Figure 32. During the engine cool down period before a schedul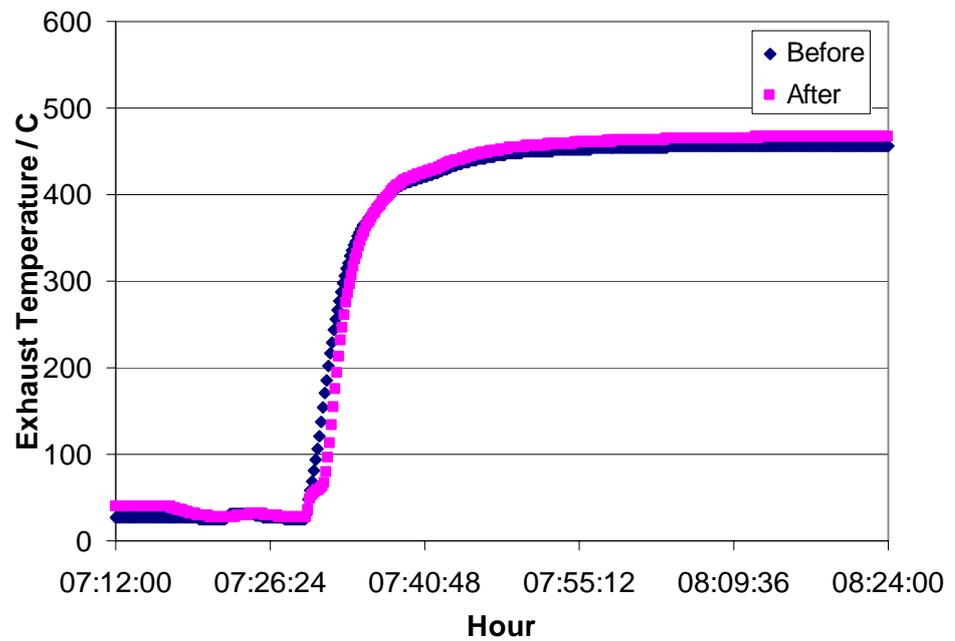ed stop the engine exhaust temperature rises to 550 °C from a level of 460 °C at stable operation. The data were collected on the 27th May 2004 shortly after the commissioning of the catalyst. The Hjortebjerg catalyst showed some capabilities for oxidation of unburned hydrocarbons during the first operation hours; see Section 6.3 and Figure 14. The temperature data obtained during engine stop was, therefore, analysed for signs of increased heat generation during the engine cool down period where additional hydrocarbons were expected to be present in the exhaust. Figure 33 shows time occurrences of the exhaust temperature after the catalyst and the difference in temperature (after – before). The figure does show a small decrease in temperature difference followed by a sharp peak in temperature difference that coincides with the maximum temperature after the catalyst. However – when the occurrence in time of the sharp temperature difference peak is compared to exhaust temperature before the catalyst (Figure 34), it is revealed that the peak is due to delayed cooling of the exhaust gas after the catalyst rather than to heat arising from oxidation of hydrocarbons.

As for site Tørring the engine exhaust temperature during normal operation at site Hjortebjerg was very stable. Figure 35 only shows a small drift in temperatures of approximately 2 °C for almost five hours of continuous operation.

Due to the loss of efficiency of the catalyst towards hydrocarbon oxidation it was investigated if the temperature difference (after – before) decreased as expected. Figure 36 shows a small decrease in the order of 2 °C in normal operation temperature difference in a one-year time span. This difference is small compared to the uncertainty of the temperature measurements. If, however, the figure is taken as true value, this corresponds to approximately

75 ppm less methane combusted after one year of operation, assuming CO oxidation fraction is constant. This would change the conversion of un-burned hydrocarbons observed in the measurements performed on May 21st 2004 from 15.6 % to 11.7 % one year later. This is, when compared to Figure 14, in line with obtained results. On May 24th after 3500 hours of operation emission measurements showed 12.7 % reduction in unburned hydro-carbons.

When analyzing the total heat balance for Hjortebjerg using the data from the emission report on May 21st, 2004 theoretical calculations of the exhaust gas temperature rise in the catalyst will give 13 °C assuming no heat loss to surroundings and hydrocarbon to be methane. This is in line with the ob-served temperature rise seen in Figure 36 of 11 to 11.5 °C.
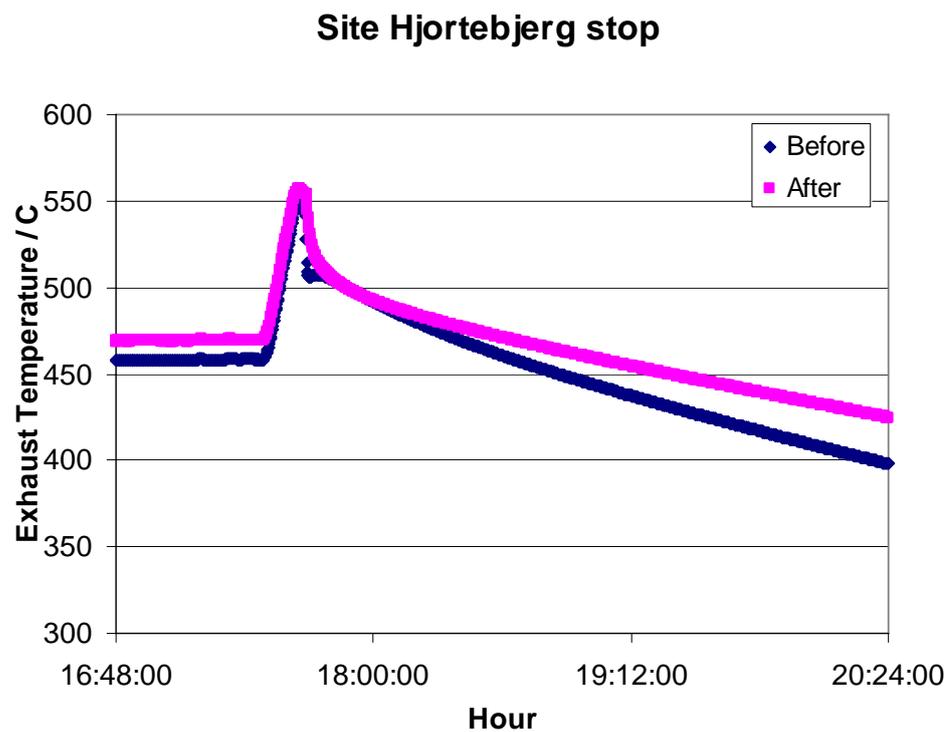
Figure 32   Temperature before and after catalyst during engine stop

Site Hjortebjerg stop
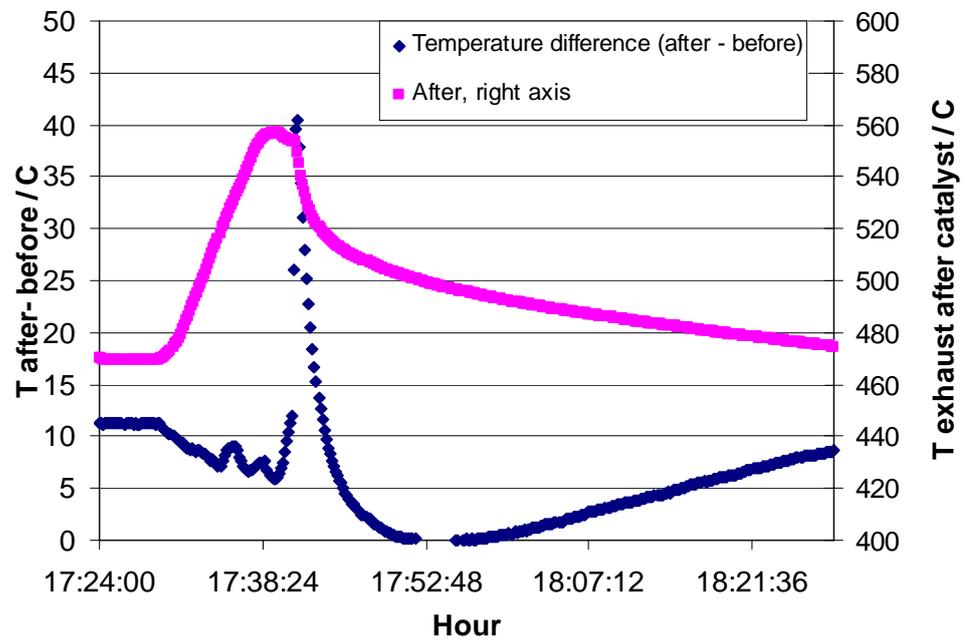
Figure 33   Temperature during stop on 27-05-2004

Site Hjortebjerg stop
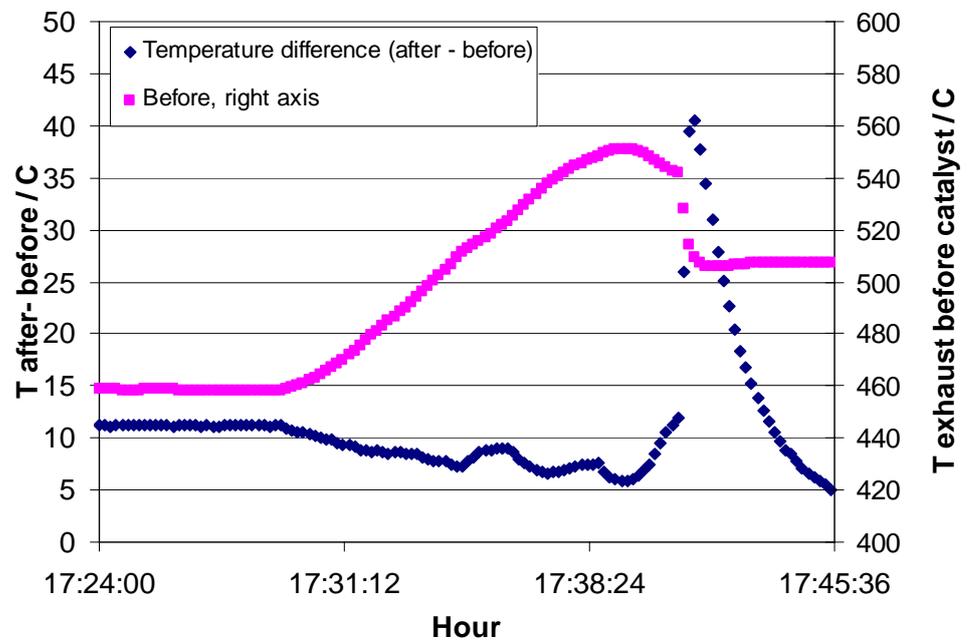
Figure 34   Temperature during stop on 27-05-2004

Site Hjortebjerg stable operation
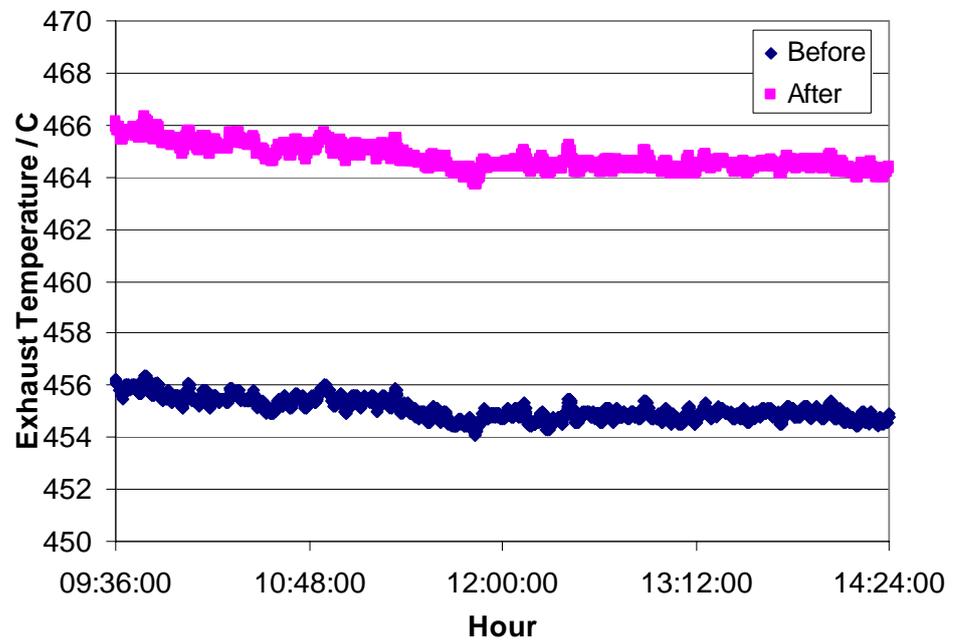
Figure 35   Temperature before and after catalyst during stable operation on 27-05-2005

Site Hjortebjerg temperature difference
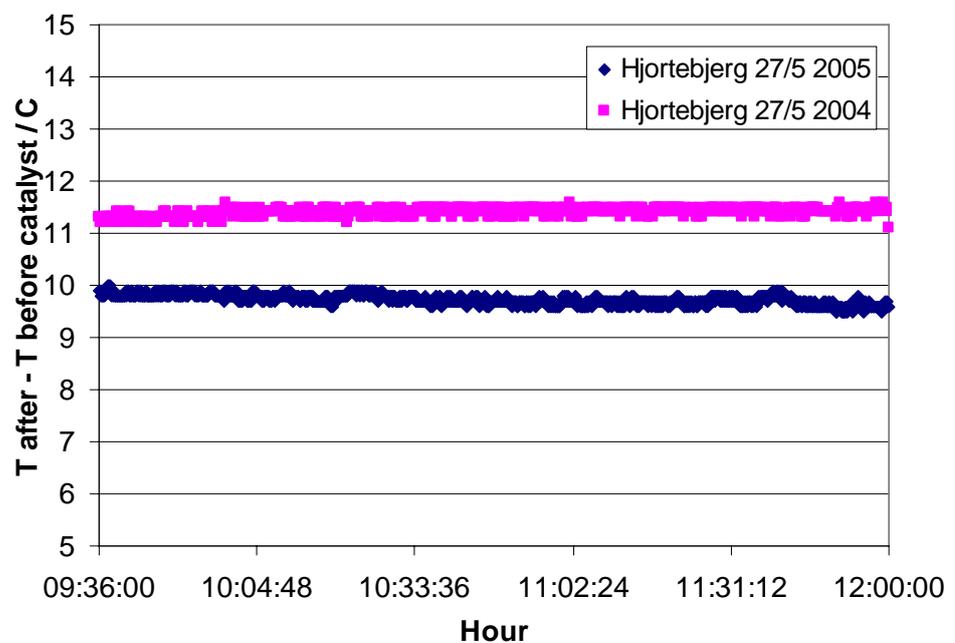
Figure 36   Temperature difference (after-before) during stable operation

7.3   Temperature during engine failure at Hjortebjerg

On May 28th, 2004 the engine in Hjortebjerg failed mechanically and lubrication oil was led into the exhaust pipe system. The temperature profile for the exhaust gas before and after the catalyst was studied in detail in order to see if the catalyst suffered extreme temperatures. Figure 37 show the temperatures relative to the engine failure. No extreme temperatures were observed, but the figure does reveal an abnormal temperature profile for the before catalyst exhaust gas from engine failure and the following 200 seconds.

The catalyst was not soaked in oil, and the emission results collected later in the project did not indicate any influence on the catalyst efficiency.

Site Hjortebjerg engine failure
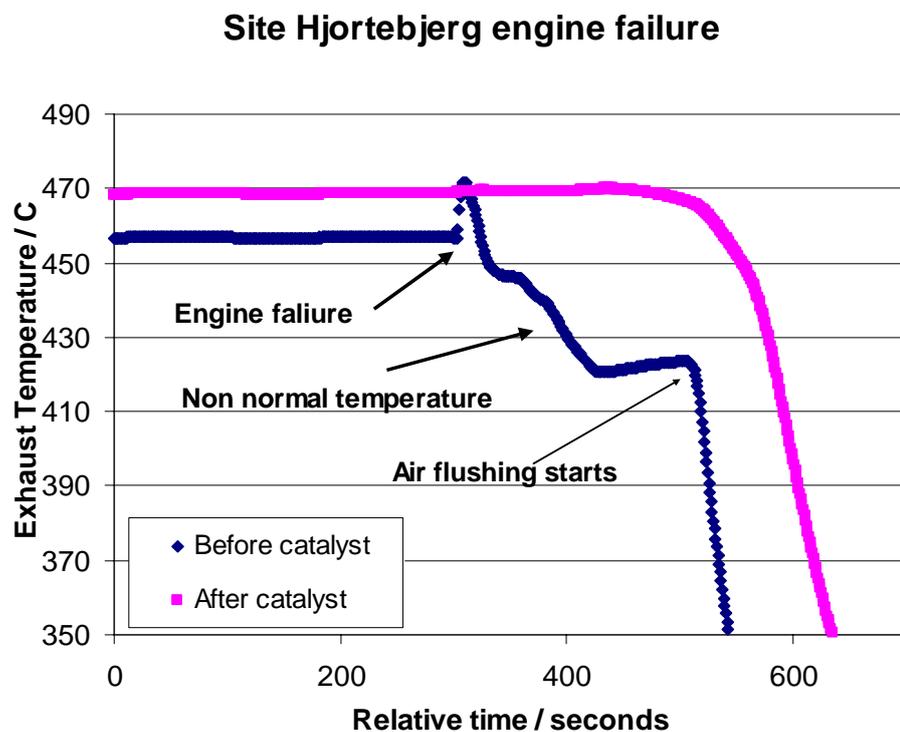
Figure 37   Exhaust gas temperature during engine failure

8 Discussion

8.1 Other methods for formaldehyde reduction

A part of the project focused on different methods for formaldehyde reduction. A progress report was issued for this work (in Danish) by Michael Ørtenblad /8/. The following section summarises the conclusions from this work including formaldehyde catalysts and various alternative solutions to help reduce formaldehyde emission from natural gas fired gas engines. In the discussion of the different solutions both technical and economical information is presented. For each technology the functionality, technical and economical advantages and setbacks are described and the investments and operating costs are summarised.

The emission of formaldehyde from natural gas fired gas engines in Denmark is reported to be around 800 tons per year or approximately 70 mg/m^{3}n @ 5 % O_2 /1/. Formaldehyde is a carcinogen (causes cancer) and is dangerous to people as well as to the environment. Reduction of formaldehyde emission is therefore desirable and the emission from natural gas fired gas engines is regulated by the Danish government.

8.1.1 Catalytic reduction

Catalytic reduction of formaldehyde is carried out by passing the flue gas through one or more catalytic sections covered by a catalytically active material. The active material converts the formaldehyde and to some extent other emissions and odour as well. The final life time of the catalyst elements are still to be determined. The field test showed that the catalyst does lose efficiency as the operation hours accumulate.

The investment costs for a formaldehyde catalyst for a 1 MW$_e$ gas engine are about 70.000 DKK. The operating costs are estimated to be 25.000 DKK per year. The major advantage of using catalytic oxidation is that when properly installed it is a simple process without any problematic operation issues.

8.1.2 Absorption technology

Absorption naturally takes place when the concentration of an organic compound in gas phase is higher than the equilibrium concentration of the same

compound on a liquid surface. Absorption of formaldehyde from exhaust gas into water can be carried out in a gas scrubber. A reduction of 66 % of the formaldehyde concentration in the gas phase has been observed in pilot-scale tests. The possible reduction is expected to rise upon optimization of the process. No long term operation data are available for the process.

The investment costs will be around 400.000 DKK for a 1 MW_e gas engine and the annual operating costs are estimated to be 100.000 DKK.

Absorption is a quite simple industrial process, but it can have more operational problems than the catalyst. The main disadvantage is the costs of operation, due to consumption of water and costs to treat the formaldehyde after absorption.

8.1.3   Biological treatment of exhaust gas

Biological abatement technology can be used to decompose unwanted compounds in flue gas from gas engines. This branch is relatively new in the field of emission control, for which reason only few examples and documented solutions exist. The few examples where biological abatement technology is used to reduce the formaldehyde content of a flue gas show that it is possible to obtain reductions as high as 99 %.

The costs associated with biological systems depend greatly on the specific process and can be difficult to estimate. A typical process plant is expected to have investment costs close to 500.000 DKK for a 1 MW_e gas engine and the annual operating costs will be in the range of 30.000 DKK. The main disadvantage is the lack of documentation.

8.1.4   Incineration

Incineration of flue gas from gas engines is carried out in a burning process where the organic compounds are oxidized by raising the temperature. The compounds are either burned thermally or the process can be helped by a catalyst which lowers the needed reaction temperature. Currently, only one regenerative thermal oxidizer is installed on a large gas fired power plant in Denmark. This oxidizer reduces the formaldehyde content in the flue gas by approximately 90-95 %.

A regenerative thermal oxidizer is a heavy investment and the price for the oxidizer alone is about 1-1.5 million DKK per installed MW_e. The operating costs consists mainly of expenses for supplementary firing to keep the oxidizing process going and are estimated to be low at 15.000 DKK per year. The main disadvantage is the high costs and the main advantage is that the incineration process also removes almost everything else that can burn, including methane, other aldehydes, CO and odour. If the emission of other combustibles is high, heat recovery after incineration may improve the operating costs significantly, depending on gas prices.

8.1.5   Regenerative catalyst

Other catalytic solutions than the specific formaldehyde catalysts mentioned earlier exist. These solutions are developed to cope with other emissions but are found to reduce the formaldehyde emission as well. Recuperative catalysts are designed to reduce unburned hydrocarbons in flue gas most effectively. These systems also reduce the formaldehyde content in the flue gas with a high efficiency of more than 95 %. The RECCAT system is expected to have lower investment costs than the incinerators for plants below 5 MW_e. The operation costs will be very low. The major disadvantage is that the process is not yet well proven, only a few thousands hours of field operation is available. Field test is ongoing at a gas engine site.

8.1.6   Other possible formaldehyde reduction

Another possibility is the combination of an SCR (Selective Catalytic Reduction) catalyst and a CO catalyst which is used on engine exhaust used for greenhouse fertilization. It is well documented that this solution reduces the formaldehyde emission by 97 %. The main disadvantage is the investment and operation costs, but the system will also reduce NO_x and CO.

Naturally, the investment costs for these solutions vary according to the solution chosen and how extensive the installation is. Table 12 summarises the key figures for the methods and Table 13 summarises the effect on different engine emissions.

Table 12 Key figures of various formaldehyde reduction technologies.
Please refer to /8/ for original references to the methods.

Technology	Reference (year)	Type	Commercially available	Investment costs[1] DKK	Operating costs[1] DKK	Operating winnings DKK	Design size MW$_e$	Capacity m^3/h	Reduction %
Formaldehyde catalyst	Südchemie (2004) /4/	Oxy-cat.	Yes	unknown	unknown	-	unknown	unknown	60-40
Formaldehyde catalyst	Johnson Matthey (2004) /4/	Oxy-cat.	Yes	130.000	25.000	-	2	8.750	95-85[5]
Absorption	DGC (2003) /1/	Scrubber	-	400.000	100.000	unknown	1	4.500	66[3]
Biological abatement	BIP Ltd. (1997) /2/	Bioreactor	Yes	2.750.000[4]	33.000	-	-	60.000	99
Incineration	Nordborg (1999) /5/	Thermally recuperative	Yes	3.800.000	15.000	200.000[2]	6	39.500	93
Incineration	KonoKogs (2004) /6/	Thermally recuperative	Yes	1.000.000	15.000	200.000[2]	1	4.500	> 95
Other catalysts	RECCAT (2004) /3/	Recuperative UHC catalyst	Yes	1.000.000	50.000	250.000[2]	1	4.500	> 99,5
Other catalysts	Gartneri (1997) /7/	SCR + CO	Yes	1.000.000	140.000	-	1	4.500	> 97
Other catalysts		CO Oxy-cat.	Yes	~ 100.000	~ 25.000	-	1	4.500	< 30

[1] Investment costs listed are exclusive of installation and buildings. Operating costs cover only operation; depreciation is not included.
[2] The 200.000 DKK are only valid if the heat produced can be realized. If not, only the 100.000 DKK are valid through a lower consumption of gas.
[3] The low degree of reduction is a result of an unoptimized pilot project.
[4] The investment costs do not include equipment for heat exchanging the flue gas down to max. 30 °C.
[5] 95-85 % reduction applies to 0-10.000 hours of operation.

Table 13 Formaldehyde reduction technologies and their efficiencies in reducing other emission species. Please refer to /8/ for details.

Technology	Reduction, %						
	Formaldehyde	NO_x	UHC	CO	Odour	Lubricating oil	Other aldehydes
Formaldehyde catalysts (This study has show a large dependency on catalyst make)	50 – 95	-	< 15	> 90	~ 40	?	30-70
Absorption	~ 66	-	-	-	?	+	+
Biological abatement[1]	> 99	-	-	-	-	-	+
Incineration	> 93	-	99	> 50	~ 75	~ 65	> 93
Recuperative UHC catalysts	> 99	-[4]	> 98	> 99	+	+	+
SCR + CO catalysts	> 97	> 95	~ 25	> 99	?	?	> 97
CO catalysts	+[2]	-	-	> 95[3]	?	-	+[2]

[1] Micro organisms are chosen specifically according to the type of emission to be reduced.
[2] A strong CO-catalyst is expected to be able to remove formaldehyde emission.
[3] The efficiency depends on the dimension of the catalyst.
[4] The technology indirectly reduces NO_x emission because the engine can be adjusted to give a low NO_x emission. This results in a high UHC emission which is removed by the catalyst.

8.2 Positive effect on other emissions

The field test has revealed that the catalyst has an additional oxidizing effect on the other aldehydes present in the exhaust gas. This is very positive since the acetaldehyde and acrolein in many cases exceed the allowable emission set by the recommendations "Luftvejledningen" /3/. Both acetaldehyde and acrolein are emissions looked upon with great concern causing very low emission limits. Following the recommendation in /3/ and B-value in /4/ would set the emission limit to 2.5 mg/m^3 for acetaldehyde and 0.25 mg/m^3 for acrolein. The emission regulation will come into force for mass flow above 25 and 0.5 g/h of mass flow, respectively. Table 14 summarises regulations and Table 15 summarises the emission at the three sites where there is enough data to give significance to the numbers.

Table 14 Regulation and emission for acetaldehyde and acrolein

Component	Mass flow limit	Emission limit
	g/h	mg/m^3
Acetaldehyde	25	2.5
Acrolein	0.5	0.25

Table 15 Regulation and average emission for acetaldehyde and acrolein before catalyst

Site	Emission		Approximate mass flow	
	mg/m^3 @ 5% O$_2$, dry		g/h	
	Acetaldehyde	Acrolein	Acetaldehyde	Acrolein
Hjortebjerg	5.4	0.7	29	3.7
Jetsmark	5.9	0.3	43	2.2
Tørring	3.5	0.1	46	1.3

This means that all three plants would have had problems with the acetaldehyde emission limit and the two first plants would have had problems with acrolein if the catalyst were not installed. Data from the emission factor study suggest that almost all larger plants will have problems with the acetaldehyde and approximately half the engine plants will exceed the acrolein limit operation without exhaust gas cleaning.

The formaldehyde catalyst is also active in oxidizing CO. Most engines will already be equipped with a CO catalyst. If the formaldehyde catalyst is applied CO emission will be much lower that demanded by regulation.

The catalyst is also active in odour reduction, which might be useful since the new regulations on gas engines now set forward odour emission limits for gas engines. The effect on odour is only documented with a few measurements, but the effect was nevertheless statistically significant. There is a large spread among the odour reduction results, and we do not know why. For this reason use of the catalyst to reduce the odour will need to be done with care and consideration.

The formaldehyde catalyst showed only minor oxidation of the unburned hydrocarbons, and after some operation hours the effect seemed to disappear. There was, however, some effect on the non-saturated hydrocarbons (ethane, acetylene and propene).

Whether the catalyst has an effect on lubrication oil emission or not was not resolved by this study due to measuring difficulties.

8.3   Costs of catalyst and plant economics

The costs of the catalysts applied in this study were in the cost range of slightly above the costs for CO catalysts used today, see Table 12. However, as described in Section 6.1.1, the need for catalytic activity for the formaldehyde removal to be sufficient up to 40.000 hours of operation will raise the costs depending on the formaldehyde emission limit. Additional costs will come from catalyst installation. Implementation of catalysts on plants where they are not present today will to a certain level be possible at a reasonable cost. If, however, the demanded space for catalyst installation is not present at the site today, costs will increase rapidly due to additional costs for larger buildings and/or additional work changing the engine site layout with heat exchangers and exhaust gas piping. Since most engine sites in the future will be on the liberalised power market, additional investment costs will influence the power price these plants can offer on the market. If, due to higher costs, they lose a market share on the power market, consumers using district heating will have to carry the additional costs selling power at lower than cost prices or alternatively producing the heat on boilers. The influence on district heating prices will be very individual from plant to plant depending on plant layout.

Technically, also the pressure drop will influence the possible catalyst dimensions at each engine. The allowed pressure drop will depend on engine make and plant layout.

Costs of catalysts can be expected to follow world market prices on precious metal (Pt, Pd …) and US$. Both figures can be quite volatile.

8.4   Best available technology

When the possibilities outlined in Table 12 are compared, the preferred technology for removal of formaldehyde will be the direct catalytic methods. The only uncertainty in using the oxidation catalyst will be the long-term (above 12.500 hours) performance, which remains to be proven. From the results obtained in this study it seems likely that catalyst producers will be able to produce the catalyst needed to do the job at a reasonable price. The catalyst will at the same time solve problems with CO, acetaldehyde, acrolein and partly odour. Another reason for choosing a direct catalyst system is that the system is simple and without supporting equipment. This is beneficial in terms of low operating and maintenance costs and problem-free operation for plant owners.

Depending on power and natural gas prices and if the need for reduction of unburned hydrocarbons arises, the RECCAT and the incinerator solutions become interesting for plants that can utilise the heat. This will be true for most Danish engine sites. The RECCAT technology remains to be proven in long-term field operation while the incinerator has shown good results in full scale for many years at a single plant in Denmark. At current prices for natural gas and power, the expected costs of using the RECCAT and incinerator solution for removal of formaldehyde, acetaldehyde and acrolein will be larger that the expected costs of using the direct oxidation catalyst solution.

9   Conclusions

Two years of field test using catalysts designed for formaldehyde reduction have shown that formaldehyde reduction is possible. One type of catalyst showed 95 % decreasing to 85 % formaldehyde reduction after 10.000 hours of operation. The other type of catalyst showed a lower degree of oxidation, from 60 % in the beginning to 40 % at 10.000 hours of operation. Both suppliers of catalysts claim that it will be possible to deliver catalysts, which can cope with the expected demands, but this will be at higher costs than those catalysts used in the field test. Also, additional installation costs may arise due to larger catalysts.

The use of direct formaldehyde catalysts will be beneficial regarding emission of other aldehydes with emission regulations. The catalysts showed a good degree of oxidation on acetaldehyde and acrolein.

Using formaldehyde catalysts will lower the emission of CO significantly below the emission limit. The effect on odour is significant, but there is a large spread in results, which therefore need to be used with care.

When comparing direct catalysts with other technological solutions for formaldehyde reductions, the result is that the oxidation catalyst will be preferable both from a technical and an economical point of view. If, however, gas prices increase further and if focus turns to the large emission of unburned hydrocarbon, both the incinerator and RECCAT solutions become more interesting. At current energy prices the most economical solution for formaldehyde reduction is the oxidation catalyst.

10 References

/1/   Eltra Emission mapping study for decentralised power produc-
        tion. Results of PSO project 3141, 2002. All six parts of the re-
        ports are available from www.energinet.dk.

/2/   Regulation 720/1998 (in Danish). Regulation on gas engine
        emissions in Denmark. Has recently been replaced with regula-
        tion 621/2005.

/3/   Luftvejledningen (in Danish). Recommendations for handling
        air pollution from all types of industry including energy plants.
        Recommendation 2/2001.

/4/   B-værdivejledningen (in Danish). Recommendations for dilution
        demand for chimneys. Recommendation 2/2002.

/5/   Lipari, J.F. and Swarin, S.J.; j. Chrom. 247, 1982, pp 297-306.

/6/   Kristensen, P.G.; Measurement of Carbonyl Compounds, DGC
        1998.

/7/   Measurement of Air Toxic Emissions from Combustion Equip-
        ment at Natural Gas Processing Plants. GRI report prepared by
        Radian International LLC, 1997, report no. GRI-96/0009.1 and
        GRI-96/0010.2.

/8/   Reduction methods for formaldehyde in gas engine exhaust (in
        Danish), M. Ørtenblad, DGC, 2006.

Appendix A

Contact information on participants in expert monitoring group meetings

The following table shows the participant list for the expert monitoring group meetings. Each person on the list has participated in minimum one expert monitoring group meeting. DGC wishes to acknowledge the support and suggestions to the project by these committed participants.

Name	Organisation	e-mail
Allan Jakobsen	Catcon	asj@catcon.dk
Ari Souminen	Wärtsilä	ari.suominen@wartsila.com
Asger Hansen	Enmaco	asger.l.hansen@emo.geveke.com
Bent Iversen	Wärtsilä	Bent.Iversen@wartsila.com
Carsten Nielsen	DONG/Gasselskaberne FAU GI	cdn@dong.dk
Christoph M. Heinisch	Johnson Matthey GmbH	heiinic@matthey.com
Erik Nørregaard Hansen	FDKV	mail@fdkv.dk
Erik Thomsen	Miljøstyrelsen	et@mst.dk
Gerko van Dijk	Gasunie (Hanwel)	G.H.J.van.Dijk@gasunie.nl
Helga Moos	Brancheforeningen	bdk@helgamoos.dk
Henk Busschers	Hanwel	h.busschers@hanwel.com
Henrik Andersen	DGC	han@dgc.dk
Henrik Jørgensen	Wärtsilä	
Henrik Lilja	Håndværksrådet	Henrik_Lilja@hvr.dk
Jean Pierre Fatio	Caterpillar Inc./Enmaco	
Jens Hylling Kristensen	Jenbacher	Jens.Kristensen@ge.com
Jens Møller Jacobsen	Pon Power	jens.m.jakobsen@pon-cat.com
Jesper Greve Jensen	Jenbacher	jesper.jensen@GEJenbacher.com
Johan Boij	Wärtsilä Finland	johan.boij@wartsila.com
Keld Skærbæk	Rolls-Royce	keld_skarbak.nielsen@rolls-royce.com
Kent Jensen	Wärtsilä	
Kim Behnke	Eltra/Energinet.dk	kim.behnke@energinet.dk
Kim Larsen	Rolls-Royce	Kim.larsen@rolls-royce.com
Lise Nielson	Eltra/Energinet.dk	lise.nielson@energinet.dk
Michael Ready	Caterpillar Inc./Enmaco	
Michael Ørtenblad	DGC	moe@dgc.dk
Michele Schiliro	Deutz Power Systems	schiliro.m@deutz.com
Morten Krebs Christen-sen	CatCon (Süd-Chemie)	mkc@catcon.dk
Niels Bjarne Rasmussen	RECCAT	info@RECCAT.dk
Ole K. Jensen	DFF	ok.jensen@dff.dk
Panagiotis Daskalopoulos	Euromot	Panagiotis.Daskalopoulos@vdma.org
Per G. Kristensen	DGC	pgk@dgc.dk
Per Lyngholm	Jenbacher	per.lyngholm@GEJenbacher.com
Renny van der Keyl	Johnson Matthey plc	vander@matthey.com
Steen D. Andersen	DGC	sda@dgc.dk
Steen Vestervang	Energinet.dk	STV@energinet.dk
Stefan Euler	Süd-Chemie	stefan.euler@sud-chemie.com
Tim J. Benstead	Johnson Matthey plc	benstt@matthey.com
Vibeke Vestergaard	Miljøstyrelsen	vvn@mst.dk

Appendix B

Danish EPA method for formaldehyde testing: MEL-12 (in Danish)

The method has been developed by the Reference Laboratory sponsored by the Danish EPA. The Reference Laboratory sets standards for emission measurement methods to be used in Denmark for documenting regulated emissions and advises the Danish EPA and industry on emission measurements. Please see www.ref-lab.dk for further information.

Måling af emissioner til luften   Metodeblad nr. MEL-12

Bestemmelse af koncentrationer af formaldehyd i strømmende gas (DNPH-metoden)	
Parameter	**Formaldehyd (methanal, HCHO)**
Anvendelsesområde	Måling af formaldehyd i luftemissioner fra virksomheder.
Metode	Manuel opsamling i en dinitrophenylhydrazin-opløsning, og efterfølgende analyse ved højtryksvæskekromatografi med UV-detektion.
Referencer	VDI 3862, blatt 2, 2000 [1] (supplerende referenceliste i kap.12)
År	Revision 1 (revideret 2003) - første udgave 2002.

Indholdsfortegnelse

Måling af emissioner til luften

1. Brugervejledning til miljømyndigheder

Kapitel 8 i Luftvejledningen [2] indeholder en liste over Miljøstyrelsens anbefalede metoder til måling af luftforurening fra virksomheder (emission). Metodelisten revideres og opdateres af Miljøstyrelsens Referencelaboratorium for måling af emissioner til luften. Den reviderede metodeliste er (kun) tilgængelig www.ref-lab.dk. Ud over metodelisten udgiver Referencelaboratoriet endvidere en række metodeblade for udvalgte parametre. Disse metodeblade er i nyeste version tilgængelige på www.ref-lab.dk. Metodeliste og metodeblade sendes i høring inden udgivelse og væsentlige ændringer.

Metodelisten er beregnet til brug ved miljøgodkendelser og sagsbehandling. Et vilkår bør altid indeholde målemetode samt henvisning til metodeblad, såfremt der er udarbejdet et. Vilkår uden angiven målemetode står juridisk svagt i en eventuel klagesag.

Metodebladene er målrettet til målefirmaer og andre med specialinteresse for målinger, og giver information, på dansk, om hvordan målingerne skal udføres og hvilke særlige forholdsregler og modifikationer der kan forekomme efter danske forhold. Formålet er at sikre ensartede måleresultater samt at oplyse om særlige forhold, hvor modifikationer eller andre forholdsregler er påkrævet. For miljømyndighederne har metodebladene kun interesse i det omfang der foreligger en mistanke om at målingerne ikke er udført med tilfredsstillende kvalitet eller hvis der er tvivl om tolkningen af resultater mv. I situationer, hvor målefirmaer eller virksomheder henvender sig til myndigheden med et måleteknisk problem eller problemstilling kan miljømyndigheden have glæde af at læse metodebladet.

Metodebladet for planlægning og rapportering, MEL-01, er aldrig blevet udgivet, men er i stedet indarbejdet som en del af kapitel 8 i Luftvejledningen [2], der indeholder generelle forskrifter vedr. indretning af målested samt adgangsforhold til målestedet. Indretningen af et målested kan være et væsentligt bidrag til et måleresultats troværdighed, og bør være en del af virksomhedens vilkår. Miljømyndighederne bør således ud over de almindelige vilkår, også stille vilkår om målestedets indretning samt adgangsforhold til målestedet.

Vilkår bør i øvrigt indeholde krav til relevant produktion under præstationskontrol samt rapportering af produktionens reelle størrelse/omfang under målingernes gennemførelse. Uden et sådan krav kan præstationskontrol i værste fald være misvisende og ikke nødvendigvis et mål for den reelle emission på andre dage. Et sådant vilkår bør udarbejdes i samarbejde med virksomheden.

Når vilkår indeholder et krav om målemetode samt krav om akkrediteret måling bør der være tillid til at målingen så også er gennemført efter forskrifterne i metodeblad, standard mv. Der kan dog være situationer, hvor miljømyndigheden ønsker at vurdere kvaliteten af målingen eller ønsker at vurdere om målemetoden rent faktisk er egnet til formålet. Til disse formål kan metodebladet læses af miljømyndigheden specielt med fokus på følgende emner:

- – Målestedets indretning
- – Dokumentation for produktionsforhold under målingen
- – Anvendt prøvetagnings system (materiale og temperatur)
- – Feltblind

Måling af emissioner til luften   MEL-12
                                                            Formaldehyd

– Varme fugtige gasser (er der taget højde for risiko for kondensation)
– Interferens
– Isokinetisk udsugning (skal ligge mellem 95 % og 115 % af korrekt isokinetisk flow ved alle partikelmålinger)
– Antallet af travers punkter
– Laboratorieblind

Usikkerhed.
Det er krævet i ISO 17025 [3], som laboratorierne akkrediteres efter, at laboratorierne beregner usikkerheden på målingerne[I]. Usikkerheden på målingen angives i rapporten.

I Luftvejledningen [2] kapitel 5.4.1 er det angivet, at: *Emissionsvilkåret anses for overholdt, når det aritmetiske gennemsnit af alle enkelt-målinger udført ved præstationskontrollen er mindre end eller lig med kravværdien.* Usikkerheden indgår således ikke i vurderingen af en præstationskontrol, og det er op til den enkelte tilsynsmyndighed om den opnåede usikkerhed på målingen er tilfredsstillende.

2.   Anvendelsesområde

Dette metodeblad beskriver måling af emissioner af formaldehyd til luften fra afkast med strømmende gasser. Med afkast menes her skorstene, ventilationsafkast eller kanaler, gennem hvilke der udsendes varm eller kold gas til atmosfæren – f.eks. i forbindelse med gas- eller træfyringsanlæg, gasturbiner, forbrændingsmotorer, lakeringsanlæg, røgerier, vulkaniseringsanlæg, plastindustri eller ved fremstilling af mineraluldsprodukter og spånplader.

Metoden kan samtidig anvendes til måling af andre carbonylforbindelser (aldehyder og ketoner), herunder f.eks. acetaldehyd, acrolein, glutaraldehyd, butanon og acetone.

2.1 Måleområde
Fra 0,005 til 10 mg/m³(n,t) ved 60 minutters måletid. Måleområdet kan udvides ved at forøge eller forkorte prøvetagningstiden eller ved at fortynde den eksponerede prøve. Det aktuelle måleområde vil endvidere afhænge af det anvendte prøvetagnings- og analyseudstyr og –betingelser.

2.2 Begrænsninger

Der kendes kun få interfererende stoffer. Store mængder af andre carbonylforbindelser (f.eks. acetone eller butanon i blandingsfortyndere), ozon (f.eks. i forbindelse med UV-hærdning) eller nitrogendioxid (f.eks. i forbindelse med forbrændingsprocesser) kan reagere med DNPH-reagens i opsamlingsvæsken, og dermed reducere kapaciteten. Proble-

---

[I] Skal gennemføres i overensstemmelse med GUM [4], det vil sige enten ISO 14956 [5], eller de rapporter på Referencelaboratoriets hjemmeside (www.ref-lab.dk), der findes om emnet. For visse komponenter er der nyttig information i den standard der beskriver metoden. Målestedets indretning bør indgå i beregningen af usikkerheden.

Måling af emissioner til luften   MEL-12
                                              Formaldehyd

met kan normalt løses ved at forøge mængden af DNPH i opsamlingsvæsken[II], eller for-korte opsamlingsperioden, men i ekstreme tilfælde må der anvendes en alternativ måle-metode, f.eks. chromotrophsyre-metoden [6]. Nitrogendioxid (f.eks.i emissionen fra gas-eller benzinmotorer) kan give anledning til dannelse af en komponent, der kan interferere i kromatogrammet (overlap med formaldehyd-toppen), men problemet kan normalt løses med en optimeret kromatografi [7]. Ozon kan ligeledes give anledning til dannelse af in-tererende toppe i kromatogrammet. Dette problem kan forebygges ved anvendelse af en ozonskrubber, der monteres før vaskeflaskerne [8], eller ved en optimeret kromatogra-fi.

Ved måling i en atmosfære med indhold af formaldehyd på bundet form (f.eks. som hexa-methylen-tetramin, der anvendes som hærder af phenol-formaldehyd-resiner), vil der i den sure opsamlingsvæske ske en hel eller delvis spaltning til fri formaldehyd. Såfremt kun fri formaldehyd ønskes medbestemt, kan en metode med en alkalisk opsamlingsvæ-ske anvendes – f.eks. AHMT-metoden [9].

3. Princip

3.1 Prøvetagning
En delgasstrøm udsuges gennem et filter og to i serie med filteret forbundne vaskeflasker. Filteret, der kan placeres i kanalen eller uden for efter behov, kan undlades, såfremt der er tale om en partikelfri gas. Prøvetagningssystemet skal bestå af materialer, der ikke reage-rer kemisk eller fysisk med prøvegassen (normalt rustfrit stål, glas eller teflon). Ved risiko for kondensation skal prøvetagningssystemet (før vaskeflaskerne) under målingen være opvarmet til 110 °C.

De to seriekoblede vaskeflasker indeholder en absorptionsvæske bestående af en svovlsur opløsning af 2,4-dinitrophenylhydrazin (DNPH) i acetonitril. I en syrekatalyseret reaktion reagerer formaldehyd med hydrazinen under dannelse af en stabil hydrazon efter følgende reaktion:

formaldehyd   2,4-dinitrophenylhydrazin   2,4 dinitrophenylhydrazon

---
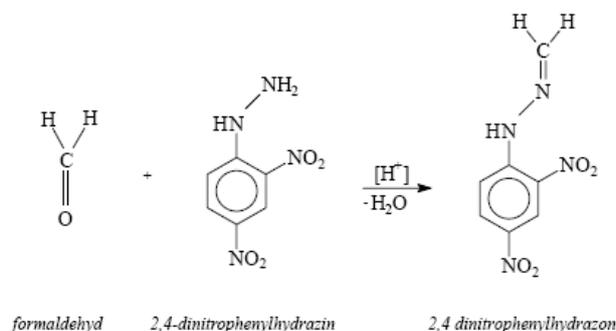
[II] Eksempelvis anbefales en DNPH koncentration på 4g/1 i 2 gange 100 ml absorptionsvæske til måling på udstødsgasser fra gasmotorer, der har et højt indhold af nitrogendioxid.

Måling af emissioner til luften

MEL-12
Formaldehyd

Vaskeflaskerne bør køles med isvand for at undgå afdampning af acetonitril. Efter vaske-flaskerne tørres den udsugede gasprøve.

Gasprøven udsuges med en pumpe efterfulgt af et flowmeter til regulering af den udsuge-de mængde, en kalibreret gasmåler samt et termometer til registrering af temperaturen. Den tørre gasmængde bestemmes ved hjælp af den kalibrerede gasmåler, som aflæses før og efter hver prøvetagning.

Optionelt kan der indskydes et manometer imellem pumpe og vaskeflasker. Derved kan et forøget undertryk (f.eks. som følge af tilstopning af filteret) identificeres. Manometeret kan samtidig anvendes ved lækagekontrol (se afsnit 3.1).

Hele prøvetagningsopstillingen kan skitseres som følger:
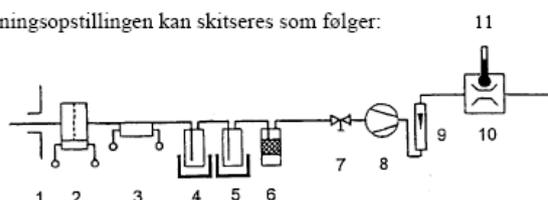
1. Prøvetagningssonde
2. Filter (kan opvarmes)
3. Prøvetagningsforbindelse (kan opvarmes)
4. Vaskeflaske (i isbad)
5. Vaskeflaske, back-up (i isbad)
6. Tørretårn (og fælde til acetonitril-dampe)
7. Gasreguleringsventil eller kritisk dyse
8. Pumpe
9. Flowmeter
10. Gasmåler
11. Termometer

3.2 Analyse

Absorptionsvæskerne analyseres uden videre forbehandling (bortset fra evt. fortynding i acetonitril) ved højtryksvæskekromatografi med UV-detektion (HPLC/UV).

Formaldehyd identificeres ud fra retentionstiden. Såfremt laboratoriet råder over en dio-de-array detektor, kan der til verifikation i tvivlstilfælde supplerende optages et UV-spektrum (sammenlignes med standard).

Koncentrationen af formaldehyd bestemmes ud fra toppens areal, og ud fra en kalibre-ringskurve baseret på analyse af absorptionsvæsker med et kendt indhold af formaldehyd.

Måling af emissioner til luften   **MEL-12**
                                                         Formaldehyd

4. Udstyr

4.1 Prøvetagning

- *Sonderør* i rustfrit stål, glas, teflon eller lign. inert materiale, der ikke reagerer kemisk eller fysisk med prøvegassen i passende længde i forhold til kanalen/skorstenens diameter.
- In-stack eller out-stack *partikelfilter* af glasfiber/kvarts, sintret metal eller keramisk materiale, der ikke reagerer kemisk eller fysisk med prøvegassen.
- *Prøvetagningsforbindelser* imellem filter og vaskeflasker samt imellem vaskeflaske og pumpe af glas, Teflon, rustfrit stål eller lign. materiale, der ikke reagerer kemisk eller fysisk med prøvegassen. Afstanden imellem kanal og vaskeflaske skal være så kort som mulig.
- *Vaskeflasker* (normalt 25-ml) af glas med sintret glasfritte D2.
- *Isbad* til køling af vaskeflasker under prøvetagning.
- *Lufttørrer* – f.eks. en tom vaskeflaske, der er fyldt med tørret silicagel (blågel). Fungerer samtidig som fælde for acetonitril-dampe
- Gastæt opvarmet *pumpe* af materiale, der ikke reagerer kemisk eller fysisk med prøvegassen. Pumpen skal være forsynet med reguleringsventil, og kunne levere 1,0 liter/min.
- Kalibreret *gasmåler*
- *Manometer* (optionelt)
- *Termometer*
- *Flowmeter* (1,0 liter/min.)
- *Barometer* til registrering af lufttryk

4.2 Analyse

- *Højtryksvæskekromatograf* (HPLC) forsynet med UV detektor (365 nm), dataopsamling og evt. med kolonneovn (35°).
- Reverse Phase analytisk *kolonne* af C18-typen
- *Guard kolonne* af samme type (anbefalet)
- *Målekolber*, 50ml
- *Finnpipetter*, 0,1-1,0ml og 5-50ml
- *2,4-Dinitrophenylhydrazin* p.a. Opbevares i tætte brune glasbeholdere. Kan evt. omkrystalliseres i acetonitril før brug. Er typisk opfugtet med 30% vand på grund af eksplosionsrisiko af den tørre hydrazin.
- *Svovlsyre* p.a., 0,5 M
- *Acetonitril*, HPLC-kvalitet
- *Methanol*, HPLC-kvalitet
- *Tetrahydrofuran*, HPLC-kvalitet
- *Kalibreringsstandard* – enten som faste hydrazoner eller som stamopløsning. Mulige leverandører er f.eks. Supelco eller Promochem. Skal være sporbar.
- *Absorptionsopløsning:* 400 mg tør 2,4-dinitrophenylhydrazin og 4,0 ml 0,5M svovlsyre fyldes op til 1,0 liter med acetonitril. Skal opbevares i tæt emballage, da den hurtigt suger formaldehyd til sig fra omgivelserne. Absorptionsopløsningen kan opbevares på køl i flere måneder.

Måling af emissioner til luften   **MEL-12**
                                                                         Formaldehyd

5. Planlægning

Se kap. 8 i Miljøstyrelsens vejledning nr. 2, 2001 "Luftvejledningen".

Proceduren foreskriver måling i ét punkt i kanalen/skorstenen. Er der risiko for lagdeling (f.eks. ved målesteder tæt på rørsammenføringer), skal målestedet flyttes til et sted med fuld opblanding. Kan dette ikke lade sig gøre, skal der under målingen traverseres over kanaltværsnittet, som ved en partikelmåling (se metodeblad MEL-02 [10]).

6. Fremgangsmåde

6.1 Samling af prøvetagningsudstyret og lækagekontrol

1. Prøvetagningssystemet samles, og ca. 15 ml[III] absorptionsvæske påfyldes vaske-flaskerne. Evt. opvarmning af prøvetagningssystemet tilsluttes.

2. Prøvetagningssystemets indgang blokeres, og pumpen startes. Såfremt prøvetagnings-systemet er tæt, vil gasmålerens tæller efter kort tid stå stille. Vær forsigtig når bloke-ringen fjernes igen!

   Som alternativ kan der indskydes et manometer imellem pumpe og vaskeflasker. Ind-gangen blokeres, og pumpen startes. Når der er opbygget et vacuum på 4-600 mbar, stoppes pumpen. Såfremt prøvetagningssystemet er tæt, vil det opbyggede vacuum ikke ændre sig (konstant visning på manometeret).

6.2 Måling

1. Gasmålerens visning aflæses og noteres.

2. Udstyret monteres på prøvetagningsstedet i et repræsentativt punkt i kanal/skorsten. Såfremt kravene til målestedets indretning i Luftvejledningen [2] er overholdt, skal der ikke traverseres.

3. Pumpen startes, og tidspunktet herfor noteres. Udsugningsflowet justeres til 1,0 li-ter/min. Med jævne mellemrum under prøvetagning aflæses gasmålertemperatur og prøvetagningsflow. Om nødvendigt justeres flowet. Under målingen skal der opret-holdes et konstant flow (±10%).

4. Efter endt prøvetagning stoppes pumpen, udstyret demonteres fra kanal/skorsten, og gasmålerens visning aflæses og noteres. Tidspunkt for afslutning af prøvetagningen noteres - prøvetagningstiden er normalt 60 minutter.

6.3 Overførsel og transport af prøver

1. Fra vaskeflaskerne overføres absorptionsvæskerne kvantitativt til 50-ml prøveflasker. Disse flasker skal være tætte, rene og fremstillet af brunfarvet glas for at undgå lys-

---

[III] Vaskeflasker beregnet til fx. 100 ml kan anvendes såfremt måleområde, væskemængde, beholder-størrelse etc. justeres tilsvarende.

Måling af emissioner til luften

MEL-12
Formaldehyd

påvirkning under transporten til laboratoriet. Evt. indlæg i skruelåget skal være af inert og resistent materiale. Prøveflaskerne mærkes entydigt. Vaskeflaskerne efterskylles grundigt med ubrugt absorptionsvæske. Skyllevæsken overføres ligeledes til prøveflasken.

2. Under eller i umiddelbar forlængelse af prøvetagningen udtages en feltblindprøve, idet der overføres ca. 25 ml ubrugt absorptionsvæske til en prøveflaske.

3. Prøveflaskerne opbevares ved max. 25°C og transporteres til laboratoriet indenfor max. 2 døgn efter prøvetagning.

6.4 Prøveopbevaring

1. Prøverne skal analyseres inden 14 døgn efter prøvetagning. Såfremt prøverne ikke analyseres omgående, skal de opbevares ved max. 5°C.

6.5 Kromatografisk analyse

1. Prøveforberedelsen skal foregå i en atmosfære, hvor der ikke findes formaldehyd eller andre carbonylforbindelser.

2. Absorptionsvæskerne overføres kvantitativt til 50-ml målekolber, der fyldes op til mærket med acetonitril, og blandes grundigt. Prøverne bør herefter være klare. En delprøve overføres til brune HPLC-vials.

3. Absorptionsvæsker fra h.h.v. prøveflaske og backupflaske samt blind- og feltblindprøver behandles separat og identisk.

4. Absorptionsvæskerne kan herefter analyseres ved reverse-phase HPLC/UV uden yderligere forbehandling. Egnede analytiske betingelser er f.eks.:

Kolonne	RP18 (f.eks. 3,9mm x 150mm – 5 μm partikelstørrelse)
Guardkolonne	RP18 (f.eks. 3,9mm x 40mm – 5 μm partikelstørrelse)
Kolonnetemperatur	35°C
Detektor	UV (evt. diode-array)
Bølgelængde	365 nm
Mobilfase 1	15% tetrahydrofuran I demineraliseret vand
Mobilfase 2	Acetonitril
Gradient	0-18 min.: 30/70 (volumen% af mobilfase 1 og 2)
	18-35 min.: 60/40
Flow	1,0 ml/min.
Injektionsvolumen	10-20 μl

Den skitserede gradient giver en god separation, og dermed mulighed for identifikation af andre carbonylforbindelser. Ligeledes separeres formaldehydtoppen fra de interferenser, som nitrogendioxid og ozon kan give anledning til. Såfremt alene formaldehyd skal bestemmes i en interferensfri atmosfære, kan gradienten udelades.

6.6 Kalibrering

En kalibrering af den samlede metode ud fra en standardatmosfære er mulig, men kræver relativt avanceret udstyr. Der anvendes derfor en kalibrering baseret på en ekstern standard, fremstillet ud fra det rene derivat (formaldehyd-2,4-dinitrophenylhydrazon).

Hydrazonen kan forholdsvis let syntetiseres af laboratoriet selv, men det kan være tidskrævende at dokumentere renheden. Derfor indkøbes denne normalt fra en kemikalieleverandør – f.eks. SUPELCO eller PROMOCHEM – enten som ren hydrazon eller som en stamopløsning i acetonitril. Tilsvarende kan købes hydrazoner af en lang række andre carbonylforbindelser.

1. Der fremstilles en stamopløsning på ca. 100 µg formaldehyd/ml i acetonitril (målt som ikke derivatiseret form). Ved fortynding med acetonitril fremstilles en standardrække i området 0-10 µg formaldehyd/ml, svarende til ialt 0-500 µg formaldhyd pr. prøve. Der anvendes brune glas og HPLC-vials.

2. Standardrækken analyseres som prøver. Standardrækken bør bestå af minimum 4 koncentrationsniveauer og vil normalt være lineær i det anførte koncentrationsområde. Stamopløsningen er holdbar i minimum 3 måneder.

Er indholdet i en absortionsvæske større end den højeste standard (10 µg/ml, fortyndes den i acetonitril og reanalyseres.

6.7 Beregning

1. Indholdet i absorptionsvæskerne bestemmes på baggrund af kalibreringskurven. Der korrigeres for blindværdier.

2. Indholdet i gasprøven bestemmes ud fra følgende formel:

$$C = \frac{m}{V * 1000} \text{ , hvor}$$

C = koncentration af formaldehyd i kanal/skorsten (i mg/m³(n,t))
m = sum af indhold af formaldehyd i prøve- og backup-absorptionsvæskerne (i µg)
V = volumen af den tørrede opsamlede luftmænde i normtilstand (i m³(n,t))

6.8 Rapportering

Den målte koncentration af formaldehyd rapporteres normalt i enheden mg/m³(n,t), hvilket betyder mg formaldehyd pr. m³ tør gas ved 0°C og 101,3 kPa.

Måling af emissioner til luften

MEL-12
Formaldehyd

7. Kvalitetssikring

7.1 Prøvetagning

- Tæthed af prøvetagningssystemet skal kontrolleres umiddelbart før prøvetagning (se afsnit 3.1).
- Gasmåler og flowmeter kalibreres regelmæssigt.
- Absorptionsvæskerne kontrolleres for indhold af formaldehyd inden udlevering til prøvetager.
- Indholdet af formaldehyd i backup-flasken må ikke overstige 5% af den samlede mængde formaldehyd. I modsat fald kan resultatet være underestimeret.
- Der udtages altid feltblind umiddelbart efter prøvetagning for at kontrollere evt. kontaminering af absorptionsvæske under prøvetagning eller transport.

7.2 Analyse

- Laboratorieblindprøver medtages for at kontrollere evt. kontaminering under oplagring eller analysen.
- Der udføres dobbeltbestemmelse – dvs. alle prøver analyseres to gange. Afvigelsen imellem dobbeltbestemmelserne bør ikke overstige 10%. Middelværdien anvendes som resultat.
- Standardkurven skal være lineær i hele måleområdet.
- Der skal anvendes kontrolprøver og føres kontrolkort for analysen.
- Der bør regelmæssigt analyseres certificeret referencemateriale for at dokumentere sporbarhed. Denne kan skaffes f.eks. fra Promochem eller LGC.
- Ved analysen skal der altid identificeres uforbrugt DNPH i prøven. I modsat fald kan reagenset være forbrugt, og resultatet underestimeret.
- Laboratoriet bør regelmæssigt deltage i præstationsprøvninger.

8. Sikkerhed

Acetonitril er akut giftigt ved indånding og hudkontakt. For at undgå forurening af omgivelserne på prøvetagningsstedet skal opsamlingsvæskerne køles under prøvetagningen. Tørreren (silica) vil opfange de dampe, der frigøres fra vaskeflaskerne, således at de ikke undslipper til omgivelserne. Såfremt silicagelen skal genbruges, skal den tørres/reaktiveres i en ovn med afsugning.

Håndtering af absorptionsvæskerne skal foregå så hud- og øjenkontakt undgås. Evt. kan der benyttes laminerede beskyttelseshandsker af 4H typen og beskyttelsesbriller. Håndteres absorptionsvæskerne i et trangt lokale uden ventilation, kan der supplerende anvendes en kulfiltermaske.

9. Usikkerhed

Rapporten skal altid indeholde en prøvetagningsusikkerhed og en analyseusikkerhed eller en samlet usikkerhed for både prøvetagning og analyse.

Måling af emissioner til luften   MEL-12
                                                                          Formaldehyd

Usikkerheden er normalt estimeret i et usikkerhedsbudget. Der henvises til DS/EN ISO 14956 [5] for beregninger af usikkerheden ved prøvetagning og analyse.

10. Rapportering

Rapporten udformes som beskrevet i kapitel 8 i Luftvejledningen [2] samt i ISO 17025 [3]. Afvigelser fra metodeblad og metoder skal angives i rapporten.

Der skal endvidere redegøres for følgende i rapporten:

- konstateret rest af uforbrugt DNPH i adsorptionsvæsken og betydningen af dette (risiko for underestimering hvis ingen rest)
- om prøvetagningssystemet er opvarmet eller ej. Hvis uopvarmet prøvetagningssystem er valgt skal der redegøres for valget.
- antallet af feltblindprøver og deres indhold af formaldehyd
- anvendelse af optimeret chromatografi pga. intereferens

11. Modifikationer

Indeværende metode indeholder en række supplerende anbefalinger i forhold til standarden, men derudover kun ubetydende modifikationer.

Måling af emissioner til luften   **MEL-12**
                                                                   Formaldehyd

12. Referencer

[1]   VDI 3862 Blatt 2: *Messen von gasförmigen Emissionen Messen aliphatischer und aromatischer Aldehyde und Ketone nach dem DNPH-Verfahren - Gaswasche-flaschen-Methode*, 2000.

[2]   Miljøstyrelsens vejledning nr. 2, 2001 *Luftvejledningen, Begrænsning af luftforurening fra virksomheder.*

[3]   DS/EN ISO/IEC 17025: *Generelle krav til prøvetagnings- og kalibreringslaboratoriers kompetence.*

[4]   DS/ISO/CEN Guide to the expression of uncertainty in measurement (GUM). 2000.

[5]   ISO/DIS 14956: *Air Quality - Evaluation of the suitability of a measurement method by comparison with a stated measurement uncertainty,* 1998

[6]   Karst U. et.al.: *Interference of Nitrogen dioxide in the Determination of Aldehydes and Ketones by sampling on 2,4 Dinitriphenylhydrazine solid sorbents,* Fresenius J. Anal.Chem 345, 1993, p. 48-52

[7]   ISO/DIS 16000-3: *Indoor Air – part 3: Determination of Formaldehyde and other Carbonyl Compounds – active sampling method,* august 1999

[8]   VDI 3862 Blatt 4: *Messung von aliphatischer Aldehyde nach dem AHMT-Verfahren,* december 1999

[9]   VDI 3862 Blatt 3: *Messen von gasförmigen Emissionen Messen aliphatischer und aromatischer Aldehyde und Ketone nach dem DNPH-Verfahren - Kartuschen-Methode,* 2000.

[10]   Miljøstyrelsens anbefalede metoder, metodeblad MEL-02: *Bestemmelse af koncentrationen af totalt partikulært materiale i strømmende gas* (www.ref-lab.dk).

12.1   Supplerende litteratur

[11]   Parmar, Sucha S. et. al: *A study of the suitability of KI denuders for ozone removal during carbonyl merasurwments,* Meas.Toxic Relat.Air Pollut. 2, 1998, p.948-955.

Måling af emissioner til luften
MEL-12
Formaldehyd

[12]   NIOSH P&CAM 125: *Formaldehyde in Air*, januar 1974

[13]   Arbetarskyddsstyrelsen: *Bestämning av formaldehyd i luft*, Metod nr. 1030, december 1982

[14]   ASTM method T05 - Rev. 1.0: *Determination of Aldehydes and Ketones in ambient air using high performance liquid chromatography (HPLC),* April 1984

[15]   Geng, A. C., Chen, Z. L.: *Determination of low-molecular-weigt aldehydes in stack gas and exhaust gas by liquid chromatography*, Analytica Chimica Acta, 1992

[16]   Goelen, E., M. Lambrechts og F. Geyskens: *Sampling Intercomparison for Aldehydes in Simulated Workplace Air.* Analyst 122, 1997, s. 411-419

[17]   Grosjean, D. og Fung K.: *Collection Efficiencies of Cartridges and Micro-Impingers for Sampling of Aldehydes in Air as 2,4-Dinitrophenylhydrazones,* Anal. Chem. 54, 1982, s. 1221-1224

[18]   Grosjean, D. og Fung K., and Atkinson, R.: *Measurements of Aldehydes in the AirEnvironment*, Proc. Air Poll. Cont. Assoc., 1980, paper 80-50.4

[19]   Health and Safety Executive MDHS 78, *Formaldehyde in air*, May 1994

[20]   Kallinger, G., Niessner, R.: *Development and laboratory investigation of a denuder sampling system for the determination of carbonyl compounds in stack gas*, Springer-Verlag, 1997

[21]   Kennedy, E. R., Teass, A. W., and Gagnon, Y. T.: *Industrial Hygiene Sampling and Analytic Methods for Formaldehyde*, American Chemical Society, 1985

[22]   Kristensen, P. G.: *Aldehydemissioner fra Gasmotorer*, Dansk Gasteknisk Center A/S, juni 1998

[23]   Lipari, J. F., og S. J. Swarin: *Determination of Formaldehyde and other Aldehydes in Automobil Exhaust with an Improved 2,4-Dinitrophenylhydrazin Method.* J. Chrom. 247, 1982, s. 297-306

[24]   Method 430, *Determination of Formaldehyde and Acetaldehyde in Emissions from Stationary Sources*, State of California Air Resources Board, 1991

Appendix C

Comments to results by "Brancheforeningen for De-central Kraftvarme" (Suppliers' organisation for decen-tralised combined heat and power production)

The following pages are prepared by the suppliers' organisation.

DGC has not been involved in the preparation of the pages, and the statements are representative of the opinion of the suppliers' organisation only.

Comments on the formaldehyde report by the association "Brancheforeningen for Decentral Kraftvarme"

General comments
The full scale field test has been performed in order to establish the best possible way to combine economical and technical aspects in the effort to reduce formaldehyde emissions in the exhaust gas from gas engines on Danish CHP plants. The project, which has been in progress for three years, was based on a very successful corporation between the suppliers, DGC and the Danish EPA. We would like to take this opportunity to acknowledge this co-orporation since it has resulted in the presentation of very highly valued facts and statistic material. In the following we shall comments on these results.

Background – Exemption
In 2002 the new formaldehyde emission limit became effective by the Danish EPA. The limit of 10 mg at 5% O_2 reference, 0°C which referred to an electrical efficiency of 30% was described in the regulation "Luftvejledningen". Unfortunately, no suppliers of gas engines or oxidation catalysts had any know-how or experience within formaldehyde reduction from exhaust gases to this low value. The only way to comply with this limit would imply an installation of rather complicated and expensive after burner equipment. The high expenses for such installations would affect the investment as well as the maintenance costs for the plant owners.

Test plants
Exhaust gas treatment by application of an oxidation catalyst is a well known technology and to a certain limit it also contributes to the reduction of formaldehyde emissions. Two of the most common brands known by gas engine suppliers in the Danish market were asked to participate in some specified tests on plants mentioned in the formaldehyde report. The two suppliers created a formula with the purpose of reducing the formaldehyde emission.

Test results
The test results based on the final measurements showed a general reduction of 41% to 86%. Furthermore, a significant reduction of other aldehydes and CO were seen. Generally, the CO reduction was limited to 1/10 of the required maximum limit as stated in the regulation referred to as "Bek. 621". The test results also show that the formaldehyde content detected in the exhaust gas, prior to treatment in the catalyst, varies among different engine types. A reduction in the odour from the exhaust gases proved as a significant additional benefit. From a supplier's point of view it is not

possible to draw a conclusion on the reduction of odour emission based on the results of this project.

Technical and practical issues for the tested solutions
For the tested solutions there are certain space requirements which may imply a new building on some plants or some undesired piping. The mentioned consequences will have a negative influence on the plant economy. A new building will involve an additional investment and undesired piping will cause a reduction in the total efficiency. Due to such investments the economical looses will continue and imply higher energy prices to the consumers of district heating. The total differential pressure in parts of the exhaust gas installation, installed for exhaust gas treatment should not exceed 10 mbar. This is due to the fact that the total energy efficiency as well as the possibility of obtaining a stable engine operation is affected by a high total back pressure in the exhaust gas system. A stable engine operation is also essential to the reduction of the exhaust gas emissions from the engine to the lowest possible level which will simplify the installation of an exhaust gas treatment system.

Economy
Without mentioning the actual cost of an oxidation catalyst constructed for the purpose of reducing formaldehyde emissions, a rule of thumb can be used as follows: An oxidation catalyst constructed to reduce formaldehyde emissions to 20 mg/Nm^3 at 10% O_2 reference, referred to 30% of electrical efficiency will amount to approx. twice the price of a CO catalyst designed for the same engine. At the "Frederiks" test plant the test results were most significant and according to the end supplier the price amounted to four times the amount of a CO catalyst designed for the same engine.

Durability
Even though the project is carried out as a full scale field test, the conclusions are however limited to some extend. By the end of the project it was not possible to draw any conclusions regarding durability of the catalyst. The individual supplier can only express their opinion of their own product. Based on several discussions we must conclude that most suppliers agree that some maintenance activities have to be carried out within the fist period of 20,000 to 30,000 operating hours where most engine brands have reached half their operating lifetime. For comparison, CO catalysts have operated maintenance free for 40,000 to 50,000 operating hours.

Design

The design of the catalyst to reduce the formaldehyde emission down to a specified level will involve a certain design margin in order to meet the warranty demand from the end customer. Taking into consideration that more factors will influence on the durability, the design margin will have to be extended. When designing the catalyst two factors must be especially considered, since the targeted emission level will always be lower than the limit, which is:

- Design margin is needed to counter soiling of catalyst (soiling will cause an additional back pressure and loss of efficiency)

- Design margin is needed to counter the observed loss of catalyst efficiency in time

If the design is prepared to observe the emission limit after e.g. 20,000 hours of operation the average of formaldehyde emission detected within the catalyst lifetime will be significantly lower than the emission limit.

Recommendation by the association "Brancheforeningen for Decentral Kraftvarme"

On the basis of the experience with formaldehyde reduction in exhaust gases from natural gas fired engines the association "Brancheforeningen for Decentral Kraftvarme" recommends the Danish EPA to propose a formaldehyde limit of 20 mg/m3 @10% O2, dry exhaust gas and 30% efficiency. The recommendation should apply for *new* gas engine installations with a total fired capacity above 5 MW.

If the above mentioned recommendation is followed it will ensure:

- Future development of CHP production in Denmark with efficient and environmental friendly new plants

- Future market competition to provide a further development in efficient and environmental friendly energy production

If a lower limit is imposed:

- Costs will increase and new sales of plants and product development will be halted causing a stop of installation of more efficient plants

- Production costs pr heat unit will increase dramatically, causing a general reduction within cogeneration potential.

It is our wish that our comments and recommendations for a future formaldehyde limit will be considered carefully by the Danish EPA.

Brancheforeningen for Decentral Kraftvarme