R e s e a r c h   R e p o r t

ENE5/33/2000


IEA/AMF Annex XIII:

EMISSION PERFORMANCE OF SELECTED
BIODIESEL FUELS -
VTT's CONTRIBUTION



**RESTRICTED**

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**Report title and author(s)**

IEA/AMF ANNEX XIII: EMISSION PERFORMANCE OF SELECTED BIODIESEL FUELS – VTT'S CONTRIBUTION

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**General Description**

IEA Advanced Motor Fuels Annex XIII "Emission Performance of selected biodiesel fuels" was carried out in 1998 and 1999. The actual experimental work of Annex XIII was conducted at both VTT Energy and Oak Ridge National Laboratory. This report is a documentation of VTT Energy's part of the Annex. A summary of the work at both ORNL and VTT will be prepared later.

**Distribution**

The Delegates of the IEA/AMF Executive Committee from Belgium (VITO), Canada (Natural Resources Canada), Finland (VTT), Japan (NEDO, LEVO), Sweden (STEM), USA (DOE, ORNL) and The Netherlands (NOVEM). In addition, the Delegates distribute the report within each Contributing Country.

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| **Approved by** | **Availability statement** |
| Nils-Olof Nylund<br>Research Manager | Restricted |

# ABSTRACT

The target of the IEA/AMF Annex XIII "Performance of biodiesel" was to perform an extensive analysis of exhaust emissions using biodiesel in new diesel engines. The participants of the project were Belgium, Canada, Finland, Japan, Sweden, USA, and the Netherlands. The work of Annex XIII was carried out both at ORNL and at VTT. This report includes only VTT's results. A summary report of the results of both laboratories will be prepared later.

The major part of the tests was carried out with a Euro 2 emission level Volvo bus engine. Tests were made without a catalyst, with an oxidation catalyst and with a CRT particulate trap. Some tests were also carried out with a medium-duty Valmet farm tractor engine and with a light-duty Audi TDI vehicle. Several test cycles were used in the tests. In addition, engine mapping tests were carried out with the Volvo and the Valmet engine. The vegetable oil esters studied were rapeseed methyl ester (RME), soy bean oil methyl ester (SME) and used vegetable oil methyl ester (UVOME). RME and SME were tested as 30% blends in European grade diesel fuel (EN590) and as neat esters. RME was also blended (30%) into Swedish Environmental Class 1 diesel fuel (RFD). The test fuel matrix also included Canadian diesel fuel blended with 10% hydrated tall oil (TO10) and an emulsion of Swedish Environmental Class 1 diesel and some 15% ethanol (EtDI).

Compared to hydrocarbon fuels, the bioesters reduced CO end HC emissions in most cases. Adding 30% ester in the EN590 fuel did not affect the $NO_x$ emission significantly, whereas neat ester resulted in an increase of around 10% in the $NO_x$ emission. When 30% ester was blended into the RDF fuel, the $NO_x$ emission increased by some 5% with the bus and the tractor engine, but decreased by about 5% with the TDI vehicle. The EtDI fuel resulted in a lower $NO_x$ emission than the EN590 fuel with the bus engine, but a higher emission with the TDI vehicle. The effect of esters on the formaldehyde emission was not significant with the bus and the tractor engine, but an increase was observed for the TDI vehicle.

Clear reductions in PM emissions were noted with almost all technologies when esters were blended into the EN590 or RFD fuel. Black smoke was low with bioester fuels. The EtDI fuel reduced PM emissions compared with the EN590 fuel.

The particulate matter consists of, i.a., black carbon, soluble organic fraction (SOF) and sulfates. Using bioesters in the bus engine effectively reduced the "black carbon" portion, while the SOF was higher with bioesters than with the base fuel. However, this SOF portion can be reduced by using an oxidation catalyst. Altogether, significant PM reductions can be achieved when combining bioester fuels and an oxidation catalyst. Aftertreatment devices, which include an oxidation element (oxidation catalyst and CRT pariculate trap), promote the generation of sulfate from fuel sulfur. In this respect the low-sulfur bioesters are advantageous. The particulates of the TDI vehicle were "dry" (low SOF portion) with all fuels, and no significant differences between the fuels were observed regarding SOF or sulfates.

A reduction in particulate SOF and semivolatile phase PAH emissions was observed for the bus engine without the catalyst when esters replaced the EN590 fuel. However, the

30% RME blend did not give benefits regarding PAH emissions compared to the RFD fuel. In the tests with a catalyst the overall PAH level was so low that no fuel effects were observed. The same applies to the catalyst equipped Audi TDI vehicle.

Mutagenic activity was studied using the Ames test. Neat esters reduced the mutagenicity of particulate SOF compared to the EN590 fuel in the tests without catalyst, but not when compared to the RFD fuel. The effects of the 30% ester blends and the EtDI fuel were not significant.

The Ames results with oxidation catalyst were very low. The oxidation catalyst significantly reduced the mutagenicity of particulate SOF, except for RFD and RFD/RME30 fuels, which had low levels regardless of the aftertreatment applied. There were some indications that the neat RME gives slightly better results than the EN590 fuel. The CRT particulate filter gave no significant benefits regarding the mutagenicity of particulate SOF compared to the tests without catalyst. This might be explained by the formation of nitro-PAH compounds.

Particle size distribution was studied with the bus engine (without catalyst). RME resulted in lower mass of particulates in the main peak area (around 0.1 µm) than EN590 or RFD fuels. The number of particles below 56 nm was lower for RME than for the EN590 fuel. However, the lowest number of particles in that range was observed for the RFD fuel.

In summary, the general trends for bus and tractor engines were higher $NO_x$, but lower CO, HC and particulate emissions for bioesters than for diesel fuel. The particulates generally seemed to be less harmful for neat bioesters than for diesel fuel. The changes in emissions were not as significant when 30% bioester blends were compared with EN590 or RFD as when neat esters were used. The only difference between the esters was seen with the TDI vehicle: some benefit for the UVOME fuel regarding CO, HC and aldehyde emissions when compared with the RME and SME fuels. The new TDI light-duty technology showed an interesting result: the $NO_x$ emission was not higher for esters than for hydrocarbon fuels, which often is a problem in heavy-duty engines. The ethanol emulsion fuel gave some emission benefits regarding particulates, but this fuel was not studied as extensively as the other fuels. The hydrated tall oil blend gave worse emission figures than the other fuels, but this is believed to be due to differences in the base fuel.

# PREFACE

IEA Advanced Motor Fuels Annex XIII "Emission Performance of selected biodiesel fuels" was carried out in 1998 and 1999. Operating Agents of the project were VTT Energy and Oak Ridge National Laboratory. The participants of this cost-shared project were:

> *VITO (Belgium)*
> *Natural Resources Canada (Canada)*
> *Tekes, VTT Energy, Fortum Oil and Gas (Finland)*
> *LEVO (Japan)*
> *NEDO (Japan)*
> *STEM (Sweden)*
> *US DoE (USA)*
> *NOVEM (The Netherlands)*

The project required a lot of effort, knowledge and co-operation. VTT would like to thank the following companies and entities for participating in the project by providing fuels, aftertreatment devices and other support free of charge: *Preem Petroleum (Sweden), VITO (Belgium), Natural Resources Canada (Canada), Johnson Matthey (UK) and Erland Nilson AB (Sweden).*

In addition, the following institutes in Finland are acknowledged for their contribution to the analytical work.

> *The Finnish Meteorological Institute, particulate size distribution*
> *Tampere University of Technology, particulate size distribution*
> *VTT Chemical Technology, PAH analysis*
> *VTT Biotechnology, mutagenicity tests*

This report is a documentation of VTT Energy's part of the Annex. A summary of the work at both ORNL and VTT will be prepared later.

# CONTENTS

# ABBREVIATIONS

| | |
|---|---|
| Ames | mutagenicity test |
| "black carbon" | To simplify the discussion in this report, the portion of particulate matter other than SOF or sulfates is called "black carbon", even though it contains also other compounds (e.g. metals, nitrates). |
| BLPI | Berner low pressure impactor |
| BTX | sum of benzene, alkylbenzenes, toluene and xylenes |
| CO | carbon monoxide in exhaust gases |
| $CO_2$ | carbon dioxide |
| CRT | combination of an oxidation catalyst and a particulate trap (Continuously Regenerating Trap) |
| CVS | constant volume sampler |
| DI | direct injection |
| DNPH | dinitrophenylhydrazine |
| ECE R49 | Exhaust emission test procedure for heavy-duty engines according to Regulation No. 49 of United Nations, test method includes 13 load modes |
| EGR | Exhaust Gas Recirculation |
| ELPI | Electrical Low Pressure Impactor |
| EN590 | diesel fuel according to EN590 spesification |
| EtDI | ethanol containing diesel fuel |
| Euro | European exhaust emission test for light-duty vehicles according to directive 70/220/EEC (driving cycle in amendment 91/441/EEC) |
| FC | fuel consumption |
| FID | flame-ionisation detection |
| FTIR | Fourier Transform Infrared |
| FTP75 | emission test cycle according to US Code of Federal Regulation, Title 40, Part 86. |
| GC | gas chromatography |
| HC | total hydrocarbons in exhaust gases |
| HD | heavy-duty |
| HD cat | HD engine equipped with oxidation catalyst designed for fuels up to 500 ppm sulfur content |
| HPLC | high performance liquid chromatography |
| IC | inter-cooled |
| IDI | indirect injection |
| na | not analysed |
| LD | light-duty |
| MS | mass spectrometry |
| $NH_3$ | ammonium |
| NO | nitric oxide |
| $NO_2$ | nitrogen dioxide |
| $NO_x$ | nitrogen oxides in exhaust gases |
| $N_2O$ | nitrous oxide, dinitrogen oxide, laughing gas |
| ox. cat | oxidation catalyst |
| PAH | polyaromatic hydrocarbons |
| PM | particulate matter emission |

| | |
|---|---|
| ppmS | sulfur content, parts per million |
| PSD | particle size distribution |
| PUF | polyurethane foam |
| RFD | Swedish Environmental Class 1 diesel fuel |
| RME | rape seed oil methyl ester |
| SME | soy bean oil methyl ester |
| SMPS | Scanning Mobility Particle Sizer |
| $SO_4$ | sulfates |
| SOF | soluble organic fraction of particulate matter |
| TC | turbocharged |
| TCDD | dioxin receptor binding affinity |
| TO | hydrated tall oil |
| UVOME | used vegetable oil methyl ester |
| VOE | vegetable oil ester |
| w/o cat | without catalyst |

# 1    INTRODUCTION

There is a great interest in biodiesel in many areas, both in Europe and in North America. In Europe, pure rapeseed methyl ester (RME) is commercially available as a transportation fuel in countries like Austria and Germany. Some engine manufacturers like VW for light-duty vehicles and Valmet (Sisu Diesel) for off-road applications allow RME to be used within normal warranty conditions.

Biodiesel can be based on a variety of feedstocks. Most European activities are based on rapeseed. In the US, there is also considerable interest in soy methyl ester (and soy ethyl ester). Canada and Finland are interested in byproducts of the pulp and paper industry, for example, tall oil. Countries like Belgium and Japan are interested in used vegetable oil esters.

Vegetable oil ester (VOE) is a very flexible alternative fuel. Many diesel engines can use it as such, although there might occur some problems with elastomer compatibility, etc. VOE mixes readily with ordinary diesel fuel, and VOE can therefore conveniently be used as a blending component for diesel fuel.

A lot of information on biodiesel has been published. However, the engines used in many experiments and demonstrations have been old, high-emitting farm tractor diesel engines. The fuel effects on engine performance and emissions vary with engine technology. This is especially true when exhaust gas aftertreatment is used for emission reduction. Little is known about the detailed composition of emissions from biodiesel-fueled engines. In most published reports biodiesel has been compared with heavy sulfur containing diesel fuels. Even the most recent studies include only a limited number of fuel alternatives, engine concepts, and analysis data. Extensive analysis data for different engine alternatives and unregulated emissions do not exist.

As shown by IEA AMF Annex V, the fuel generally has a greater impact on the unregulated than on the regulated emissions. Also in the case of biodiesel, the analyses should be extended to special emission measurements including particulate composition.

The Bioenergy Agreement of IEA has activities on health effects testing of biodiesel (medical tests). The work on biodiesel within IEA Advanced Motor Fuels presented in this report will feed additional information also to the Bioenergy Group activities.

At the IEA Advanced Motor Fuels (AMF, formerly Alternative Motor Fuels) Executive Committee (ExCo) meeting held in June 1996, both Oak Ridge National Laboratory (ORNL) of U.S. and VTT Energy of Finland independently presented closely related pre-proposals on new biodiesel activities. The main objective in both proposals was to carry out extensive tests to characterise biodiesel exhaust emissions in detail. Hence, the ORNL and VTT representatives decided to join forces. At the ExCo meeting held in Charleston, USA in March 1997, a decision to start a new Annex was taken. The final written approvals from the partners were received during the fall of 1997 and after that the work on Annex started.

The objective of the task was to produce emission and performance data on biodiesel and diesel-biodiesel-blends in different types of diesel engines. Advanced diesel engines of different sizes and for different applications were used for testing. Some of the test engines were equipped with the exhaust gas aftertreatment devices. The fuel matrix contained regular and reformulated diesel fuels as a reference. Special attention was given to the measurement of unregulated emissions and analysis of particulate composition. The task shows the influence of biodiesel and biodiesel blends on emissions in comparison with conventional and improved diesel fuel qualities in modern diesel engines. It also shows the fuel effects on diesel exhaust aftertreatment devices.

The general scope of the task is summarized in Figure 1.
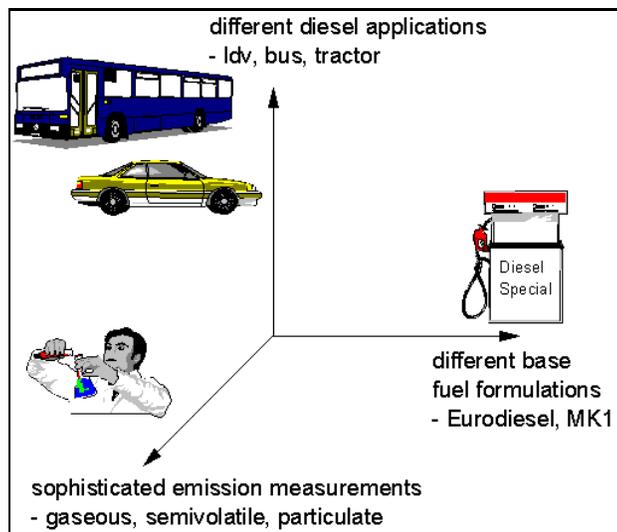


*Figure 1. The general scope of the task.*

The results can be used as input data for biodiesel suitability assessments for different applications and different markets. The work does not deal with production or cost of biodiesel or other details of economics of the fuels.

# 2    CONCISE LITERATURE REVIEW

## 2.1    GENERAL

The literature review was not included in the scope of this task. However, the target of this Annex was to have an extensive analysis of exhaust emissions using biodiesel in new diesel engines. Thus it was necessary to review what has been published during the recent years. A summary of the literature concerning exhaust emissions with biodiesel fuels is given in Table 1. Studies prior to 1996 are included only if containing relevant data on unregulated emissions or new engine technologies. More work than listed here has been carried out, e.g., in several

national programmes. However, all data is not readily available. The major part of the data listed here originates from the most known sources (SAE Papers and scientific journals).

A lot of data has been generated on regulated emissions with biodiesel for Euro 1 emission level and older engines. The newest studies have clearly shifted towards extensive emission analysis matrixes. The test engines, however, still tend to be rather old. Only a few public reports were found on Euro 2 level engines. Even less has been reported on the emissions of TDI light-duty vehicles.

The emission performance, especially the $NO_x$ emissions, varies depending on how the engine is tuned. An increase in $NO_x$ emissions switching from diesel to pure biodiesel can, at least to some extent be compensated for by retarding the injection timing. In the following review only those studies where engine parameters remained unchanged, i.e. the engines were in standard conditions, were taken into account. Emission legislation in general would not allow tuning engines manually for individual fuels.

## 2.2    REGULATED EMISSIONS WITH BIOESTERS

In 1996 Krahl et al. published a review of the effect of rapeseed oil and rapeseed oil methyl ester compared with diesel fuel on exhaust gas emissions [1]. They cited a number of studies including IDI and DI engines run according to several test cycles (FTP, 13-mode test, 5-mode test and MVEG/ECE15 test). They concluded that CO and HC emissions were generally lower with RME than with diesel fuel, and that $NO_x$ emissions increased by about 10%. No changes in mass PM emissions were observed for DI engines when switching fuels, but in almost all IDI cases a reduction of 20 - 40% in PM emissions were seen with RME. The soot number  was reduced by around 40% with RME.

A number of other studies published after this review confirm the trends regarding regulated emissions [2, 3, 4, 5, 6]. However, some studies have reported opposite results concerning the $NO_x$ emission. One study found reductions of $NO_x$ emissions in two direct-injection, turbocharged pick-up trucks [7]. Another study with a DDC Series 60 heavy-duty engine also reported reductions of both $NO_x$ and PM with bioesters [8]. One new study reported somewhat reduced $NO_x$ and higher PM with bioester [9].

One interesting comment on particulate matter results was made by Chang et al., who noticed that biodiesel is more sensitive to sampling conditions (dilution ratio and filter temperature) than conventional diesel. The results also differed a lot depending on load conditions (lower PM for biodiesel at high load but higher PM at low loads) [10]. One could assume that even contrary results might be obtained for biodiesel if, for example, the temperature of the particulate filters varies a lot between the tests with biodiesel and conventional diesel.
The new heavy-duty technology (Euro 2 emission level for Europe, common-rail or other new technologies) has not been covered extensively in the biodiesel studies. There are, however, some results also with Euro 2 level engines. One study was

carried out with a heavy-duty bus engine with several aftertreatment alternatives [11]. It was observed that the $NO_x$ emission increased slightly with RME, but the difference was generally more or less insignificant (below 5%). The PM emission decreased clearly with biodiesel both with and without aftertreatment alternatives. CO and HC emissions decreased with RME in the tests without catalyst, but in the tests with catalyst the differences between the fuels were insignificant.

A study with a modern heavy-duty engine, Volvo D12A 380EC96, was reported by Grägg [12]. RME was compared to the Swedish Environmental Class 1 diesel fuel. Lower CO, HC and PM emissions were observed for RME, but the $NO_x$ emissions were higher. These examples demonstrate that the Euro 2 engines follow the same general trend as the older engines in response to biodiesel.

The effects of biofuels on the emissions of light-duty vehicles have been studied much less than those of heavy-duty engines. This is probably a result of the very common "farm tractor" attitude towards biodiesel. Very little data was found on biodiesel fuels in conjunction with light-duty direct injection technology. For light-duty vehicles the trend regarding $NO_x$ and PM emissions is not as clear as for heavy-duty engines. However, most light-duty studies resulted in slightly higher or unaffected $NO_x$ emissions but lower particulates for bioesters (Table 1). One study with a DI van reported very small differences in $NO_x$ emissions at several temperatures [24]. The PM emission decreased at normal temperature, but increased at low temperatures with bioesters.

IEA AMF Annex V and X reports [13, 14] covered the performance of biodiesels in a TDI vehicle. The Annex V report also presented results with other light-duty diesel technologies. In the Annex V work RME was blended with Swedish Environmental Class 1 fuel. Thus this study combines both new engine technology and new fuels. For the IDI vehicles with and without catalyst the changes in $NO_x$ and PM emissions between Swedish Environmental Class 1 and a blend with RME were too small to make any conclusions. No signficant differences were observed in the $NO_x$ emission with the TDI vehicle, but the PM emissions decreased with the RME blended fuel. In Annex X only a limited number of emission tests were carried out. The trend was no change or a slight decrease in $NO_x$ emissions with a RME blend. PM emissions decreased significantly with the RME blend.

## 2.3    UNREGULATED EMISSIONS WITH BIOESTERS

In 1996 Krahl et al. found limited data on unregulated emissions for their review, and the aftertreatment alternatives were not discussed at all. However, aldehydes and PAH emissions with biodiesel have been studied quite extensively, and some information on mutagenicity and particulate size distribution is available as well [15, 16, 17, 18, 19, 20, 21, 22].

The general trend in aldehyde emissions is an increase when switching to biodiesel. However, some reports state that RME does not affect aldehyde emissions (Table 1).

It is well documented that the soluble organic fraction (SOF) of the particulates is higher with biodiesel than with diesel fuel in older engines (Table 1). On the other hand, the insoluble fraction ("black carbon") is significantly lower with biodiesel [4, 6, 12, 20, 21, 23, 24, 25]. The reason for the reduced insoluble fraction with bioesters may be increased availability of oxygen for the combustion process, which results in improved soot oxidation [25]. The increase in the SOF fraction may be due to poor fuel evaporation and heavy, fuel related organic compounds that remain intact through combustion [20]. An oxidation catalyst can reduce the SOF portion of particulates. Thus it has been stated that even if the particulate emission increases when older engines without a catalyst are tested on biodiesel, the particulate emissions might decrease when switching to biodiesel from conventional diesel if the engine is equipped with an oxidation catalyst [24].

Reductions in particulate associated PAH emissions with RME have been reported in most studies (Table 1). It seems, however, that the differences in PAH emissions between bioesters and base fuels are not very significant, especially for new heavy-duty engine technology [11, 12]. It has been demonstrated that even the exhaust gases from engines running on fuels totally free of aromatics contain PAH compounds originating from in-cylinder pyrosynthesis and/or vaporised lube oil PAH [26]. Some studies including also semivolatile PAH analysis reported that no clear differences can be found in the PAH emissions, or that PAH emissions might even increase with RME in some cases [12, 21].

One study with a Renault 21 TD vehicle included a wide range of analysis covering also 1,3-butadiene and nitro-PAH compounds [19]. It was stated that 1,3-butadiene and nitro-PAH emissions were reduced with RME. In another study no differences were observed for 1-nitropyrene between biodiesel and base fuel [21].

Most studies have reported a reduction in mutagenicity with bioesters (Table 1). Once again, the difference seems to be more of less nullified or even contrary when new engine technology is used [12].

The traditional way to estimate particulate emissions is by total mass emission. However, the particulate size distribution is also of interest, not least regarding health effects. The particulate size distribution is expressed as number, mass or in some cases also as volume distribution. Normally diesel exhaust gas is considered to have two main modes of particles: nucleation mode (10 - 56 nm) and accumulation mode (56 nm - 1.0 $\mu$m) [20].

A couple of recently published studies also include particulate size distribution measurements for biodiesel fuels. Bagley et al. reported that particle volume concentrations for biodiesel were some 45 - 65% lower compared to base fuel [21]. It has been debated that losses in volatile material during particulate size distribution measurements might be more significant for bioesters than diesel fuel due to the fact that aerosols from esters have a greater fraction of volatile material [20]. Schröeder et al. reported that biodiesel increases the number of small (nucleation mode) particulates. These particles, however, can be removed with an oxidation catalyst [22]. On the other hand, he reported that the oxidation catalyst increases the number

of particles below 15 nm. As mass distribution, only very little difference between the fuels was observed.

## 2.4     ETHANOL BLENDED WITH DIESEL

Most of the resent research work on diesel/ethanol blends has been carried out in Sweden.

A heavy-duty Scania DSC engine was tested with and without an oxidation catalyst with various fuels [27]. The test cycle was a modal bus cycle. The addition of ethanol to base fuel increased CO, HC and $NO_x$ emissions, while the PM emission decreased. Particulate associated PAH compounds were lower for ethanol blends. Nitro-PAH compounds, mutagenicity and TCDD (dioxin receptor binding affinity) were also measured, but no conclusions from the fuel effects on these emissions were drawn.

Another study with the same type of engine, Scania DSC, was carried out with the ECE R49 test cycle [28]. An increase in HC and aldehydes was observed, while CO decreased and no significant change was seen in $NO_x$ when using an ethanol containing fuel.

In previous IEA AMF work (Annex X) a bus engine meeting the Euro 2 requirements was run according to ECE R49 test with different fuels. On diesel-ethanol blends it was noticed that CO and HC emissions increased, but $NO_x$ and PM emissions decreased [14]. In the same study, another heavy-duty engine was also tested, and the results were similar for CO, HC and particulates. When the diesel-ethanol blend was tested in a TDI passenger car it was observed that the $NO_x$ emissions behaved differently: the changes were small, but rather to the direction that there was an increase in the $NO_x$ emission. A similar trend was seen for the second heavy-duty engine.

*Table 1. Selected literature data of the effect of bioesters on exhaust emissions from diesel engines and vehicles.*

| Engine technology | Equipped with | Test | NOx | PM | Aldehydes | BTX | SOF | PAH in PM SOF | Muta-genicity | PSD other | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **HEAVY-DUTY** | | | | | | | | | | | |
| IDI and DI | - | a) | + | -- | +++ | -- | | -- | | | 1 |
| DI | - | ECE R49 | + | 0…-- | + | | + | | - | | 17 |
| DI | - | 5 loads H&J | ++ | + | ++ | ns | + | - | - | x | 15 |
| DI | - | 13 and 5 loads | Schröder | + | + | | | - | | x | 22 |
| IDI | - | transient | | - | Bagley | | + | - | b) | x c) | 21 |
| IDI | ox. cat. | transient | | - | Bagley | | + | - | b) | x c) | 21 |
| IDI | - | transient | - | - | - | | + | Purcell | - | x c) | 20 |
| Scania DSC | - | trasient and R49 | + | + | - | - | mtc | - | - | c) | 18 |
| DI, Euro 2 | - | ECE R49 | ns | -- | | | | ns | | flolev | 11 |
| DI, Euro 2 | ox. cat. | ECE R49 | + | -- | | | | ns | | | 11 |
| DI, Euro 2 | CRT | ECE R49 | ns | -- | | | | ns | | | 11 |
| DI, Euro 2 d) | - | ECE R49 | ++ | -- | | | | | | mtc | 12 |
| DI, Euro 2 d) | - | ETC, FIGE | ++ | - | -- | | | ns | ns or + | x c) | 12 |
| | | | | | | | | | | | |
| **LIGHT-DUTY** | | | | | | | | | | | |
| IDI (Renault TD) | EGR | MVEG | (-…)+ | -(…+) | - | - | | - | - | Port | 19 |
| IDI (Vento TD) | ox.cat. | MVEG | + | -- | + | | | -- | | Weid | 16 |
| IDI (van) | - | transient | - | + | | | + | - | | Schr | 9 |
| DI (van) | EGR, ox.cat. | MVEG | ns | -- | + | | | - | | Jou2 | 24 |
| TDI | EGR, ox.cat | FTP | ns or - | - | | | | | | AnX | 14 |
| TDI d) | ox. cat. | transient | ns | - | | | | | | AnV | 13 |
| TDI | EGR, ox.cat. | transient | + | - | | | + | ns | | | 25 |

**-** reduction in emission      **+** increse in emission      **ns** not significant

**a)** several cycles: 13-mode, 5-mode, FTP, MVEG, ECE15      **b)** not enough data for fuel comparison   **c)** also other analyses of unregulated emissions included, e.g. nitro-PAH, semi-PAH, ozone forming potential, TCDD.   **d)** compared with Swdish Environmental Class 1 fuel

# 3    OVERVIEW OF THE PROJECT

The tasks at VTT Energy were divided into several parts. In the preparatory phase VTT visited Oak Ridge National Laboratory to prepare the final proposal of the project. In the next phase the base fuels and fuel components were obtained from different sources. The blends were prepared at VTT Energy. The most important fuel properties were analysed.

Engine mapping tests were carried out with both Volvo and Valmet engines using two fuels to study how the emissions vary under different load conditions.

The Japanese test cycle was run with the Volvo engine (w/o aftertreatment) using two fuels to correlate emission levels and changes in emissions between the fuels against the European test cycle.

The heavy-duty engine testing according to ECE R49 test with the Volvo DH10A-285 bus engine represented the bulk of VTT's test program. The emission performance level of this engine is well below the current European Euro 2 limit values. The engine was run without a catalyst, with an oxidation catalyst and also with a combination of an oxidation catalyst and a particulate trap (CRT). A full range of emission measurements was carried out with the Volvo engine:

- regulated gaseous emissions
- formaldehyde emission with FTIR equipment
- composition of particulates (soluble organic fraction, sulfates)
- particulate phase PAH
- semivolatile phase PAH
- mutagenicity with Ames test
- selected particulate size distribution measurements

In order to obtain a sufficient mass of particulates for the special analyses, the ECE R49 test was repeated several times with each fuel, especially when aftertreatment was used.

The medium-duty engine testing was carried out with a turbocharged Valmet farm tractor engine. Tests were run according to the European ECE R49 test procedure for regulated gaseous components and particulate mass emission. In addition, measurements with a FTIR instrument (including formaldehyde) were performed.

The light-duty vehicle tests were carried out in a chassis dynamometer with an Audi TDI passenger car representing modern diesel passenger-car technology. This vehicle is originally equipped with an oxidation catalyst, and the vehicle was run both with and without the catalyst. The baseline test procedure was US FTP75, but some tests were also run according to the European test procedure. In addition to regulated emissions, the following special emission analyses were performed:

- continuous FTIR measurement (gaseous components)
- aldehydes with HPLC
- particulate composition (soluble organic fraction, sulfates, PAH)
- semivolatile PAH.

The summary of the test matrix at VTT is shown in Table 2.

*Table 2.  The test matrix at VTT.*

| Engine | Fuels | Measurements |
|---|---|---|
| HDDI w/o cat | EN590, RFD, RFD/RME30, RME30, RME100, SME30 SME100, TO10, UVOME30, EtDI | Regulated, FTIR, PM (mass, SOF, SO$_4$, PAH, Ames), PAH in semivolatile phase, particulate size distribution (with 4 fuels) |
| | BASE**, BASE/RME30 | Engine mapping tests (regulated, FTIR) |
| | EN590, RME30 | Tests with Japanese test cycle (regulated, FTIR) |
| HDDI with ox.cat | EN590, RFD, RFD/RME30, RME30, RME100, TO10, UVOME30 | Regulated, FTIR, PM (mass, SOF, SO$_4$, PAH, Ames), PAH in semivolatile phase |
| HDDI with CRT | RFD, RFD/RME30, RME30, RME100, TO10, UVOME30 | Regulated, FTIR, PM (mass, SOF, SO$_4$, PAH, Ames), PAH in semivolatile phase |
| MDDI w/o cat | EN590, RFD, RME30, TO10, EtDI | Regulated, FTIR |
| | BASE**, BASE/RME30 | Engine mapping tests (regulated, FTIR) |
| LDDI with cat | EN590, RFD, RME30, TO10, EtDI | FTP75 test: Regulated, FTIR, aldehydes, speciated hydrocarbons, PAH* in particulates and semivolatile phase |
| | EN590, RME30 | European test: Regulated, FTIR, aldehydes, speciated hydrocarbons, PAH in particulates and semivolatile phase |
| LDDI w/o cat | EN590, RFD, RME30, TO10 | FTP75 test: Regulated, FTIR, aldehydes, speciated hydrocarbons, PAH in particulates and semivolatile phase |

*) EtDI/Audi combination did not include PAH analysis*
**) Base fuel in engine mapping tests was the Finnish low-emission diesel fuel*

# 4    TEST FUELS

The test fuel matrix included ten fuels. However, all fuels in the test matrix were not tested with all engine technologies. The bioesters selected for the task were rapeseed methyl ester (RME), soybean methyl ester (SME) and used vegetable oil methyl ester (UVOME). One blending component was Canadian hydrated tall oil (TO). The bioesters were blended with diesel fuel fulfilling the European EN590 specification (sulfur content below 500 ppm). An exception was the TO component, which was blended with the Canadien diesel fuel.

In addition to the European "base line" diesel fuel, Scandinavian reformulated Swedish Environmental Class 1 diesel fuel (RFD) was used as a reference. One of the bioesters, RME, was also blended with the reformulated RFD fuel. Also a blend of Swedish Environmental Class 1 diesel fuel and ethanol was included in the test fuel matrix. Table 3 presents the fuel matrix.

The vegetable oil esters are produced by an esterification process from vegetable oils, which are triglycerides containing different portions of fatty acids. E.g. the feedstock for RME is rapeseed oil, triglyceride, which contains around 58% oleic acid (18 carbon atoms, 1 double bond) and 23% linoleic acid (18 carbon atoms, 2 double bonds), whereas soybean oil contains 76 - 79% of linoleic acid. The feedstock materials and production process have distinct impacts on the exact composition and properties of bioesters.

The raw material for tall oil contains free fatty acids (not triglyserides as vegetable oils), diterpenic acids and some neutral components (like alcohols and aldehydes). The composition of tall oil depends on the quality of pine to some extent, but generally the main components are similar fatty acids as in the fatty acid portion of vegetable oil triglycerides (oleic, linoleic and linolenic acids). The tall oil product from Canada was hydrated tall oil, which means that it did not contain oxygen, but mainly straight-chain alkanes. It is possible to obtain products with a very high cetane number using this process [29].

The European diesel fuel was purchased from Fortum Oil and Gas Oy (former Neste Oil) in Finland. The rapeseed methyl ester was purchased from Svenska Ecobränsle Ab. ORNL provided the soy bean methyl ester, and VITO the used vegetable oil methyl ester. Natural Resources Canada supplied the diesel fuel containing hydrated tall oil. However, the neat tall oil product was not available, and thus the fuel containing TO was received as a ready blend made from the Canadian diesel fuel. In addition, the volume of the fuel was limited to three barrels.

The reformulated diesel fuel, Swedish Environmental Class 1, was provided by Preem Petroleum of Sweden. The fuel containing the Swedish Environmental Class 1 diesel fuel and some 15% ethanol (EtDI) was supplied from Sweden. The density of this fuel was 810 - 820 kg/m$^3$.

*Table 3. Abbreviations of the test fuels.*

| Abbreviation | Fuel |
|---|---|
| EN590 | European (EN 590) diesel, sulfur content below 500 ppm |
| RME100 | 100 % rape seed methyl ester |
| RME30 | EN590 containing 30 % of rape seed methyl ester |
| SME100 | 100 % soy bean methyl ester |
| SME30 | EN590 + 30 % soy bean methyl ester |
| TO10 | Canadian diesel fuel + 10 % hydrated tall oil |
| UVOME | Used vegetable oil methyl ester |
| UVOME30 | EN590 + 30 % used vegetable oil methyl ester |
| RFD | Swedish Environmental Class 1 reformulated diesel |
| RFD/RME30 | RFD + 30 % rape seed methyl ester |
| EtDI | Emulsion of Swdish Env. Class 1 diesel fuel and some 15% ethanol |

Selected properties of the test fuels are shown in Table 4. More complete analysis data is presented in Appendix 1. EtDI, TO10, RFD and RFD/RME30 fuels were the lightest fuels of the test matrix. The sulfur content of the bioesters was 80 - 90 ppm, which was higher than expected. The sulfur level of the blends of EN590 and

bioesters was close to 300 ppm. The sulfur level of RFD fuel was below the detection limit of the analysis equipment (specification for RFD is below 10 ppm). The cetane numbers of the test fuels were around 50 (±5 units). The only exception was the UVOME fuel, which had a very high cetane number (64).

*Table 4. Selected fuel properties.*

|            | Density at 15 °C (kg/m$^3$) | Viscosity at 40 °C (mm$^2$/s) | Cloud point (°C) | Sulfur (ppm) | Cetane number |
|------------|--------|-----------|-------------|--------|--------|
| EN590      | 850 | 3.1 | -9  | 403  | 51 |
| RME30      | 860 | 3.4 | -7  | 283  | 51 |
| SME30      | 861 | 3.3 | -8  | 279  | 47 |
| UVOME30    | 860 | 3.5 | -7  | 283  | 51 |
| TO10       | 827 | 1.8 | -26 | 41   | 45 |
| RME100     | 884 | 4.5 | -4  | 79   | 55 |
| SME100     | 887 | 4.2 | 1   | 82   | 53 |
| UVOME      | 887 | 4.9 | 0   | 92   | 64 |
| RFD        | 815 | 2.0 | -39 | <10  | 54 |
| RFD/RME30  | 834 | 2.5 | -22 | <20  | 53 |

In the engine mapping tests commercial Finnish low emission diesel fuel (sulfur <50 ppm) was used.

# 5    TEST ENGINES, VEHICLE AND AFTERTREATMENT DEVICES

Technical data on the engines and the vehicle tested at VTT for the biodiesel work are given in Table 5.

The Volvo DH10A is a Euro 2 emission level direct-injection 9.6 litre heavy-duty bus engine with an electronically controlled mechanical fuel pump. An engine of this kind has been used as the test engine at VTT Energy since 1996.

The Valmet 634 DSRE engine is a 7.4 litre farm tractor engine fulfilling the 97/68/EEC emission requirements for working machinery. The engine is a turbocharged direct-injection engine equipped with a rotary-type injection pump.

The Audi 1.9 TDI represents modern direct-injection diesel technology for light-duty vehicles. Audi is equipped with Exhaust Gas Recirculation (EGR) and an oxidation catalyst. One speciality of this vehicle is the needle-lift sensor, which detects the actual start of injection. Thus the closed-loop control control system can maintain start of injection-values programmed into the system. The Audi 1.9 TDI vehicle was tested both with and without oxidation catalysts.

Two aftertreatment devices were used with the Volvo engine, an oxidation catalyst (cat) and a combination of an oxidation catalyst and a particulate trap (Continuously Regenerating Trap, CRT). The aftertreatment devices were provided by Johnson Matthey (UK) through Erland Nilson AB (Sweden). The oxidation catalyst used

in these tests was planned for the European market, and thus it tolerated fuel sulfur up to 500 ppm.

The CRT was launched by Johnson-Matthey and Eminox (Sweden) some years ago. The CRT is a combination of very reactive oxidation catalyst and a particulate trap (Figure 2). Nitrogen dioxide formed in oxidation catalyst lowers the combustion temperature of particulates in the trap. While the particulates are combusted in the trap, nitrogen dioxide is converted back to nitrogen oxide. In some running conditions, when the particulate emission is low, some nitrogen dioxide slip might occur. The CRT effectively reduces HC, CO and particulate emissions. However, CRT requires a low-sulfur fuel below 50 ppm of sulfur.

*Table 5. Data on the test engines at VTT.*

|  |  | Volvo DH10A-285 | Valmet 634 DSRE | Audi TDI |
|---|---|---|---|---|
| application |  | city bus | tractor | passenger car |
| combustion system |  | direct injection | direct-injection | direct injection |
| charge system |  | TC, IC | TC | TC, IC |
| injection pump |  | in-line pump | rotary pump | rotary pump |
| control |  | semi-electronic | mechanic | electronic |
| number of cyl. |  | 6 | 6 | 4 |
| bore | (mm) | 122 | 108 | 80 |
| stroke | (mm) | 140 | 134 | 96 |
| displacement | (l) | 9.6 | 7.4 | 1.9 |
| maximum power | (kW) | 210 | 118 | 66 |
| rated speed | (rpm) | 2000 | 2200 | 4000 |
| max. torque | (Nm) | 1200 | 650 | 202 |
| intermediate speed | (rpm) | 1450 | 1250 | 1900 |
| aftertreatment |  | no / ox. cat / CRT | no | oxidation cat, EGR |



**Partikelfilter**
Avskiljning av sot och
förbränning till koldioxid
och vatten

**Oxidationskatalysator**
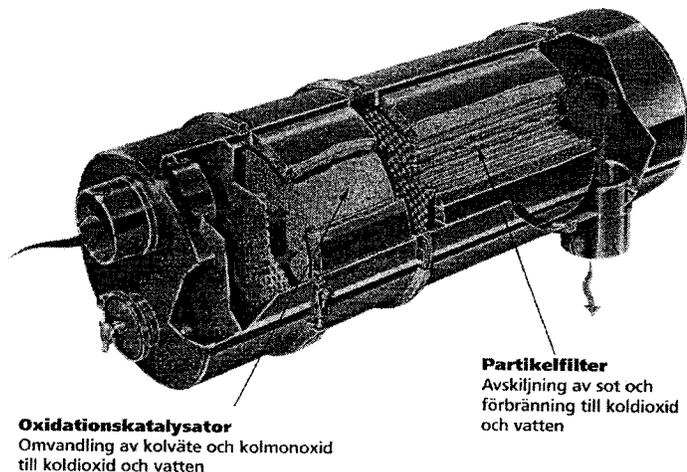Omvandling av kolväte och kolmonoxid
till koldioxid och vatten

*Figure 2. CRT aftertreatment device for heavy-duty applications.*

# 6 TEST FACILITIES AND ANALYTICAL METHODS

## 6.1 REGULATED EMISSIONS

### 6.1.1 Heavy-duty tests

All equipment used for measuring the regulated emissions (CO, HC, $NO_x$ and particulates) in the heavy-duty tests conform to the specifications for measurement systems given in Annex 4 of ECE Regulation No. 49/02. The equipment used in the tests is presented in Table 6.

A hydraulic dynamometer by Zöllner and a "PUMA Test Assistant" control system by AVL were used for running and controlling the test engine. The regulated gaseous emissions were measured with an analyser system by BOO Instrument AB. Particulates were collected using an AVL Mini Dilution Tunnel 474. In the tests with CRT catalyst, a device called AVL Smart Sampler SPC472 was used in parallel with the MDT 474 to maximise the collected particulate mass. The particulate samples were collected on Pallflex TXH120WW $\varnothing$ 70 mm filters. Semivolatiles were sampled with polyuretane foam plugs ($\varnothing$ 47 mm, height 5 cm) located after the particulate filter of the MDT 474.

*Table 6. Equipment used in the tests at VTT Energy.*

| Equipment/function | Manufacturer/type | Remarks |
|---|---|---|
| **Heavy-duty tests** | | |
| engine dynamometer | Zöllner PS1-2911 | hydraulic, 660 kW (Volvo) |
| engine dynamometer | Zöllner B-300 | eddy-current, 260 kW (Valmet) |
| dyno control & data acquisition | AVL Puma Test Assistant 5 | |
| HD regulated emissions | BOO Instrument | |
| HD particulate sampler | AVL MDT 474 | mini-dilution tunnel |
| | AVL SPC472 | smart sampler |
| HD particulate filter papers | Pallflex TX40H120WW70 | $\varnothing$ 70 mm |
| Black smoke | AVL Smokemeter 415 | |
| **Light-duty tests** | | |
| chassis dynamometer | Froude Consine 1.0 m | DC-machine, 100 kW |
| constant volume sampler | Pierburg 12,5 WT | PDP-type with heat exchanger |
| LD regulated emissions | Pierburg AMA 2000 | regulated emissions, dual-bench |
| LD particulate sampler | dil. tunnel and Pierburg PS430 | 10 " dilution tunnel and particulate sampler |
| LD particulate filter papers | Pallflex TX40H120-WW | $\varnothing$ 47 mm |

### 6.1.2 Light-duty tests

All equipment used for the measurement of the regulated emissions (exhaust dilution and collection, concentration analysis) conforms with the specifications of Code of Federal Regulations, Title 40, Part 86 (US FTP75 test) and the amendment 91/441/EEC of the Directive 70/220/EEC (European test). The equipment used in the tests is presented in Table 6.

A DC type chassis dynamometer manufactured by Froude Consine (UK) and an emission measurement system by Pierburg GmbH (FRG) were used for the measurements. Particulates were collected with a standard sampling system manufactured by Pierburg GmbH on Pallflex TXH120WW $\varnothing$47 mm filter papers. Semivolatiles were sampled with polyuretane foam plugs ($\varnothing$ 47 mm, height 5 cm) located after the standard particulate sampling system.

## 6.2    UNREGULATED EMISSIONS

### 6.2.1    Gaseous compounds

In the light-duty tests aldehydes were collected from diluted exhaust gas with DNPH cartridges. The sample of diluted exhaust gas was taken from the CVS system through a heated sample line (113 ±8 °C). The DNPH derivatives were extracted with an acetonitrile/water mixture. Altogether 13 carbonyl compounds (formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, 2-butanone, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, hexanal) were analysed with HPLC-technology (HP 1050, UV detector, Nova-Pak C18 column).

A number of unregulated compounds, including formaldehyde, were measured on-line using a Fourier Transformation Infra-Red (FTIR) system (SESAM II Fast, manufactured by Siemens AG, FRG). More than 20 exhaust components can be measured with this system at one second time interval from raw exhaust gas. However, with diesel exhaust gas the concentrations of many compounds (e.g. most of the hydrocarbons) are below the detection limit. Thus formaldehyde was the most important compound that was analysed using the FTIR instrument in the heavy-duty tests. Differences in emission results between FTIR and traditional technologies  have been observed [30]. In the work at hand, however, the FTIR technology was used mostly to screen differences, not to produce absolute results. This can be done since the deviation between parallel tests has proved to be quite small.

In the light-duty tests, hydrocarbons from $C_1$ to $C_8$ were measured from diluted exhaust gas with a HP 5890 Series II gas chromatograph ($AL_2O_3$, KCl/PLOT column). Samples of diluted exhaust gas were drawn automatically through direct lines from the same tedlar bags used for the analysis of regulated emissions. The compounds measured  were as follows: methane, ethane, ethene, propane, propene, acetylene, isobutene, 1.3-butadiene, benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene.

### 6.2.2    Composition of particulates, PAH

The sampling of the particulates and semivolatiles is described in chapter 6.1.

The soluble organic fraction (SOF) was determined by weighing the particulate samples before and after the extraction with dichloromethane (extraction for PAH analysis). The deviation of the SOF results depends on the mass of particulate matter on the filter papers. Normally the deviation is below 10%.

The analysis of sulfates using capillary electrophoresis is a routine method for engine exhaust particulates at VTT Energy. Preparation of the samples was carried out according to the IP method (water/iso-propanol extraction). Sulfate analyses were carried out from the particulate samples extracted for the PAH analysis, and this may cause some loss of sulfates if the level of sulfates is very high. Sulfates and combined water are shown in the final results. The amount of combined water in the sulfates depends on the humidity of the weighing chamber. The samples were weighed at 50% relative humidity, and thus the amount of "combined water" is expected to be 1.3 x sulfates [31]. The deviation of the sulfate analysis results is estimated to be around ±20%. However, the deviation of parallel samples in the measurements has proved to be even better than ±5% of the result, when the level of sulfates is high.

The analysis of PAH compounds with GC/MS SIM technic is an accreditated (EN45001) routine analysis at VTT Chemical Technology. The samples (particulate and semivolatile samples) were extracted with dichloromethane. Internal standards were used for all samples. Altogether, 29 PAH compounds were analysed. When the PAH results are discussed in this report, the main attention is given to 14 priority PAH compounds, which were selected based on listings in different sources (US EPA, NIOSH, VDI 3872). The PAHs analysed and the 14 PAH compounds (marked with asterix and bold-face) selected for discussion of the results were as follows:

| | | |
|---|---|---|
| naphthalene | 2-methylantracene | **\*benzo(b)fluoranthene** |
| 2-methylnaphthalene | 1-methylphenanthrene | **\*benzo(k)fluoranthene** |
| 1-methylnaphthalene | 2-phenylnaphthalene | **\*benzo(e)pyrene** |
| biphenyl | **\*fluoranthene** | **\*benzo(a)pyrene** |
| 3-methylbiphenyl | **\*pyrene** | perylene |
| acenaphthene | benzo(a)fluorene | **\*indeno(1,2,3-cd)-pyrene** |
| dibenzofurane | benzo(b)fluorene | **\*dibenzo(a,h)anthracene** |
| **\*fluorene** | benzo(b)naphtho(2,1-d)thiophene | **\*benzo(g,h,i)perylene** |
| dibenzothiophene | benzo(b)naphtho(1,2-d)thiophene | **coronene** |
| **\*phenanthrene** | **\*benz(a)antracene** | |
| **\*antracene** | **\*chrysene/triphenylene** | |

The deviation of the PAH analysis from parallel engine exhaust samples is estimated to be around ±30% of the result.

### 6.2.3 Ames test

The mutagenicity tests with Ames bacteria from particulate extract is an accreditated analysis method at VTT Biotechnology. The *Salmonella typhimurium strains* used in this study were TA98-S9 and TA98NR-S9. The strain TA98 without metabolic activation (-S9) indicates the role of direct-acting mutagenic PAHs. The bacteria strain TA98NR-S9 is the nitroreductase deficient strain, which does not response to nitrated PAH compounds. Thus, the difference between the results with these two bacteria strains indicates the role of nitrated PAH compounds on mutagenicity.

The samples are tested using five dose levels corresponding particle amounts from 0.1 to 0.8 mg/plate. Three replicate plates are used for each dose level. A linear regression analysis is carried out on the results and the numerical value of the slope is used as the measure of mutagenic activity. In some of the heavy-duty tests with the CRT filter it was not possible to obtain enough particulate mass for complete mutagenicity analysis.

The deviation of mutagenicity results from parallel engine tests are generally around ±30%.

## 6.2.4 Particle size distribution

Several measurement technologies were used for the particulate size distribution measurements to obtain as much information as possible, to compare different measurement methods and also to increase the reliability of the results. Particulate size distribution measurements were performed with the heavy-duty Volvo engine. The sampling for the particle size determination equipment was made close to the point where the total particulate sample is taken in the standardised method. The dilution ratio was adjusted to 11 with the MDT tunnel.

A Berner-type, 11-stage low-pressure impactor (BLPI), a Scanning Mobility Particle Sizer (SMPS) and an Electrical Low Pressure Impactor (ELPI) were used for the determination of particle size distributions. The BLPI measurements were carried out by the Finnish Meteorological Institute and the SMPS and ELPI measurements by the Tampere University of Technology.

The BLPI enabled the determination of particle mass size distribution over the diameter range of 0.03 - 16 μm. Particles were collected on aluminium foil impaction substrates, which were weighed before and after the collection period. The diluted exhaust gas flow through the impactor was 25 l/min and the sampling time 40 minutes.

The SMPS was used to determine the particle number distribution. The SMPS is capable of measuring particle sizes from 0.01 to 0.5 μm, and hence this instrument is especially suitable for monitoring submicrometer particles.

The ELPI instrument was used to monitor the particle number distribution from 0.03 to 10 μm. The ELPI analyser is based on aerodynamic diameter for sizing the particles, whereas SMPS uses the mobility equivalent diameter, and this leads to different information on the particles. The ELPI instrument is capable of on-line measurements.

# 7 ENGINE MAPPING RESULTS

## 7.1 TEST PROCEDURE

The full-load torque curves of the engines were determined at several engine speeds. The load points for the engine mapping tests were determined from these curves as shown in Table 7. The absolute torque and speed values obtained for the Volvo and the Valmet engines are shown in Figure 3. Weighting factors were not used in the calculation of the results.

The engines were stabilized for at least ten minutes at each load point before measuring emissions. The gaseous emissions were measured as the average of one minute at the end of each measuring period. The sampling time for particulates was 10 to 30 minutes depending on the load point.

The base fuel used for the engine mapping tests was Finnish low emission diesel fuel (winter quality). This fuel was also blended with 30% RME.

The emissions at idle are not shown in the figures of this chapter. The very low power output at idle would have meant that the specific emission values would have been too high to fit into same scale as the other results. In addition, the uncertainty of the emission results is high at idle. It can, however, be mentioned that the regulated gaseous emissions were higher for the base fuel than for the RME blend at idle. The particulate matter emission was higher for the RME blend than for the base fuel with Volvo engine, but not with Valmet engine.

*Table 7. Basis for load determination in engine mapping tests.*

| SPEED / LOAD | idle / | 50% | 60% | 70% | 80% | 90% | 100% | 102.5% |
|---|---|---|---|---|---|---|---|---|
| 0 % | PM | | | | | | | |
| 10 % | | √ | PM | √ | PM | √ | PM | √ |
| 25 % | | √ | PM | √ | PM | √ | PM | √ |
| 50 % | | √ | PM | √ | PM | √ | PM | √ |
| 75 % | | | PM | PM | PM | PM | PM | √ |
| 100 % | | | PM | √ | PM | √ | PM | √ |

√ = gaseous emissions
PM = gaseous and particulate matter emission
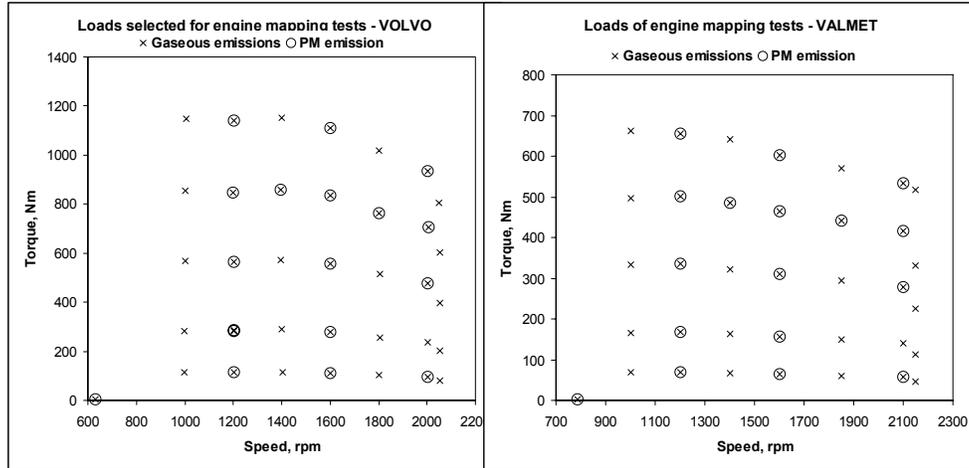
*Figure 3. Load levels used in engine mapping tests with Volvo and Valmet engines.*

## 7.2    RESULTS

The numerical results from engine mapping tests are shown in Appendices 2 - 4.

CO and HC emissions were high (as g/kWh) at low loads for both the Volvo and the Valmet engine (Figure 4). The CO map of the Valmet engine was slightly different from the map of the Volvo engine. The Valmet engine produced high CO emissions at all loads at rated speed and at maximum torque independent of engine speed, whereas the CO emission of the Volvo engine was high only at low loads.

The HC emission patterns for the two engines were quite similar; maximum HC emissions at the lowest load (10%), and decreasing HC emissions at increasing engine load. This was consistent for all engine speeds.

CO and HC emissions were lower with the RME containing fuel than with the base fuel in almost all load/speed conditions (Figure 5). This was consistent for the CO emission and only a few exceptions were seen for the HC emission at 100% load. Most noted differences were rather significant.
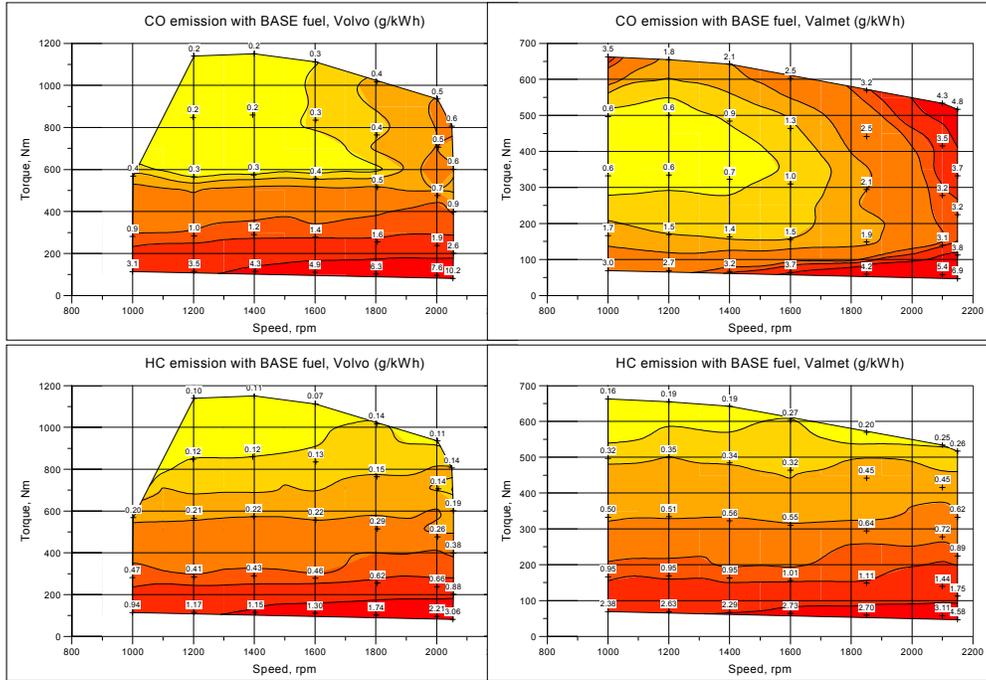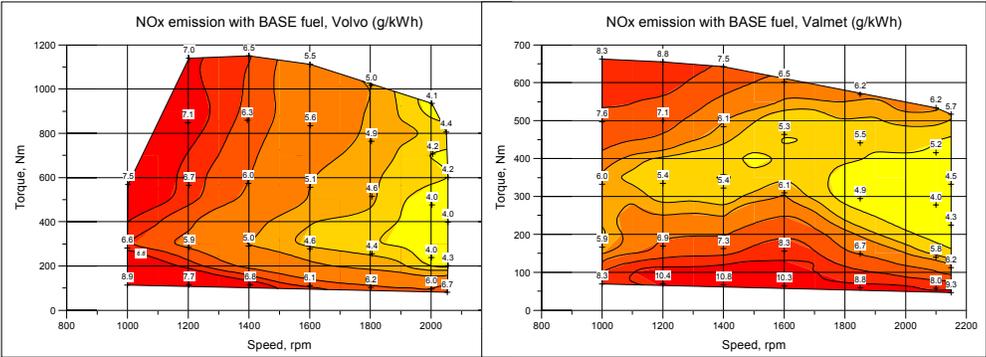
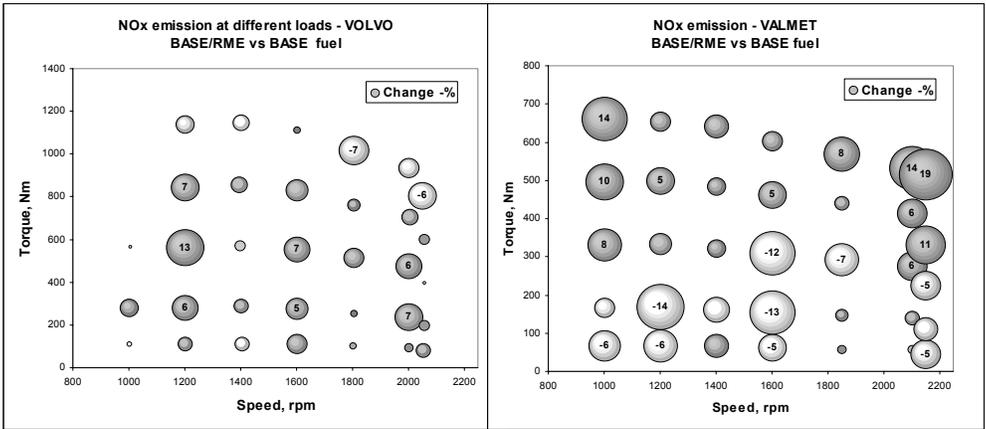*Figure 4. CO and HC emissions (g/kWh) for base fuel, Volvo and Valmet engines.*
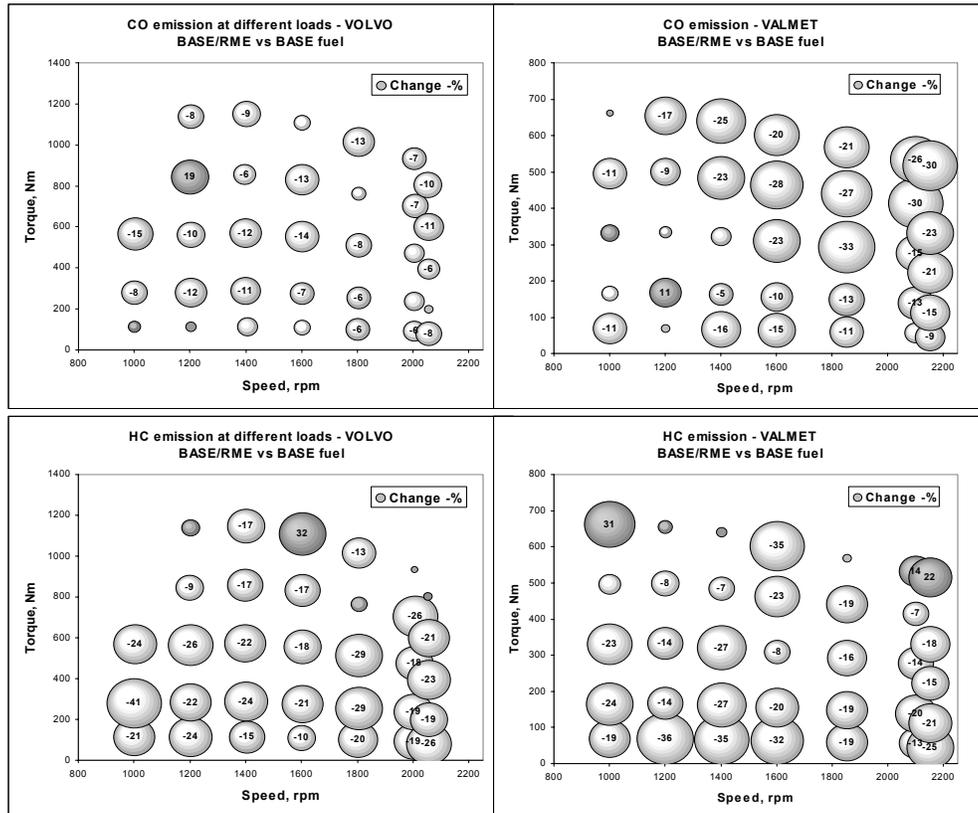


*Figure 3. Relative differences (%) in CO and HC emissions when RME blend is compared to BASE fuel. Light bubbles mean lower emissions for RME blend.*

The pattern of the specific NO$_x$ emissions expressed as g/kWh was similar for both engines (Figure 6). The NO$_x$ emission was at the highest level in low and high load conditions. The lowest NO$_x$ emissions were observed at medium loads.

The difference in NO$_x$ emission between the base fuel and the RME blend was insignificant in the most load conditions (Figure 7). With the Volvo engine, the NO$_x$ emission was higher with the RME blend at some medium load points, while the high loads gave an opposite result. The result in general was that the difference in NO$_x$ emissions between these two fuels was generally more or less insignificant.

There was, however, a small difference between the engines. The Valmet engine showed a more distinctive response to the fuel than the Volvo engine, although the differences between the test fuels were small in most load conditions also for the Valmet engine. However, the RME blend seemed to somewhat increase the NO$_x$ emissions at medium and high loads, and there was also an effect depending on engine speed. The NO$_x$ emission of the Valmet engine was lower with the RME blend than with the base fuel in low-load conditions.
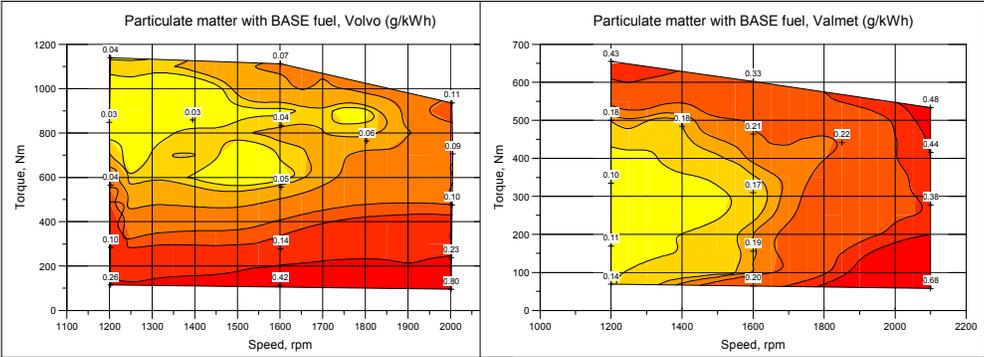


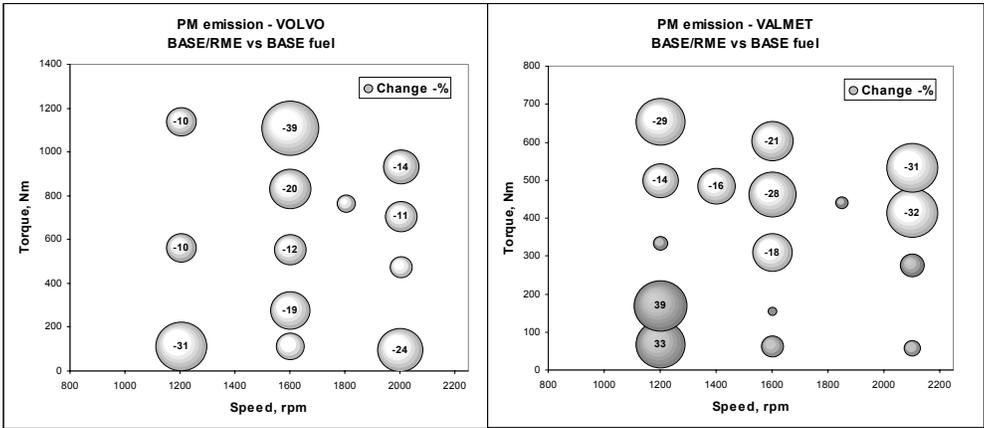Figure 4. NO$_x$ emission (g/kWh) for base fuel, Volvo and Valmet engines.



Figure 5. Relative differences (%) in NO$_x$ emission when RME blend is compared to BASE fuel. Light bubbles mean lower emissions for RME blend.

The PM emission maps for the Volvo and Valmet engines differed from each other (Figure 8). The PM emission of the Volvo engine was lower at medium and high loads than in low-load conditions. The PM emission of the Valmet engine again increased with engine load, and was relatively high at all load levels on rated engine speed. The lowest particulate matter emissions were observed for combinations of low/medium load and low/medium engine speed.

For the Volvo engine the difference in PM emissions between the fuels was in principle consistent regardless of the load (Figure 9). The RME containing fuel resulted in lower PM emission levels than the base fuel. However, the difference between the two fuels regarding the PM emission was not significant at some load modes. The idle mode is not shown in the figure, but as can be seen in Appendix 2, the PM emission at idle was higher for the RME-containing fuel than for the base fuel.

For the Valmet engine the RME containing blend resulted in lower PM emissions in medium and high load conditions at all engine speeds compared to the base fuel. In low-load conditions, on the other hand, particulate matter emissions with the RME-containing fuel were higher than with the base fuel.



Figure 6. PM emission (g/kWh) for base fuel, Volvo and Valmet engines.



Figure 7. Relative differences (%) in PM emission when RME blend is compared to BASE fuel. Light bubbles mean lower emissions for RME blend.

Specific $CO_2$ emissions and fuel consumption expressed as g/kWh were at maximum in low-load conditions. No significant differences in $CO_2$ emission were observed between the fuels. This applies for the end-use emission. Overall $CO_2$ emissions (over the whole fuel cycle) can be reduced by using biofuels. The possible total reduction in $CO_2$ emission reduction depends on how the fuel is produced, how much fossil energy is used for processing, etc. The gravimetric fuel consumption for the RME blend was higher than that for the base fuel, a direct result of differences in the energy content of the fuels (Figure 10).
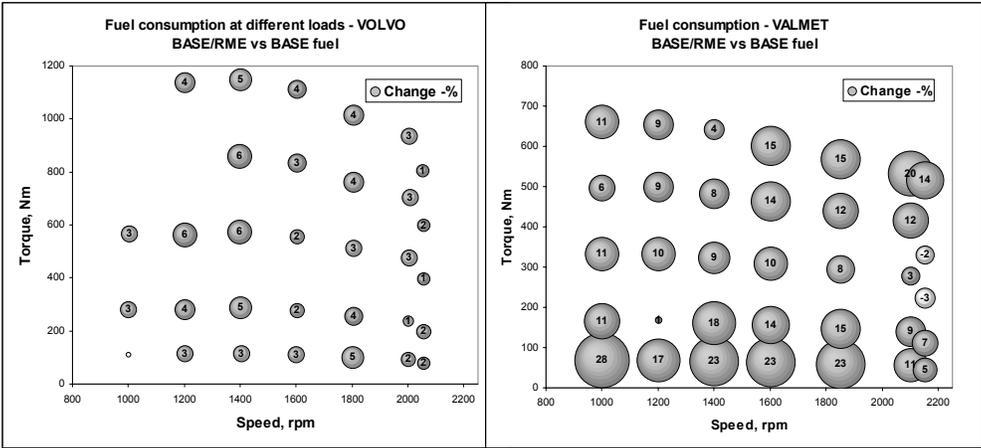


*Figure 10. Relative differences (%) in fuel consumption when RME blend is compared to BASE fuel.*

The formaldehyde emission was on the maximum level at low loads with both engines, and decreased as the load increased (Figure 11). The relative differences between the fuels were at maximum at high loads (Figure 12). The absolute emission levels at high loads were so low that the absolute differences between the fuels were not significant. However, with the Volvo engine the RME blend seemed to give somewhat lower formaldehyde emission levels than the base fuel in most operating points.
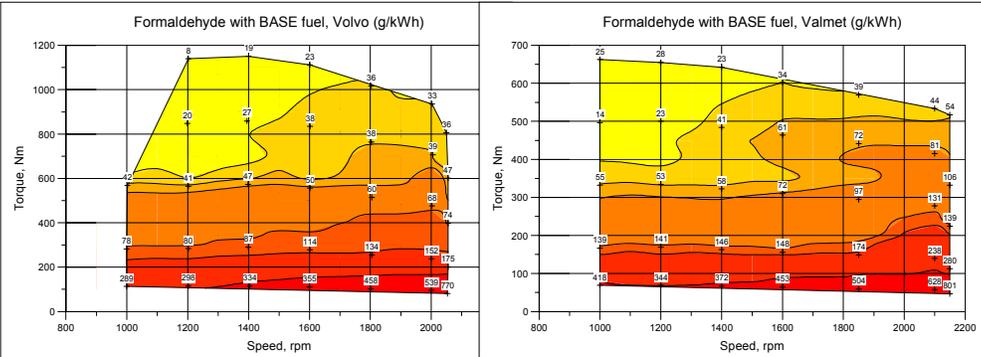


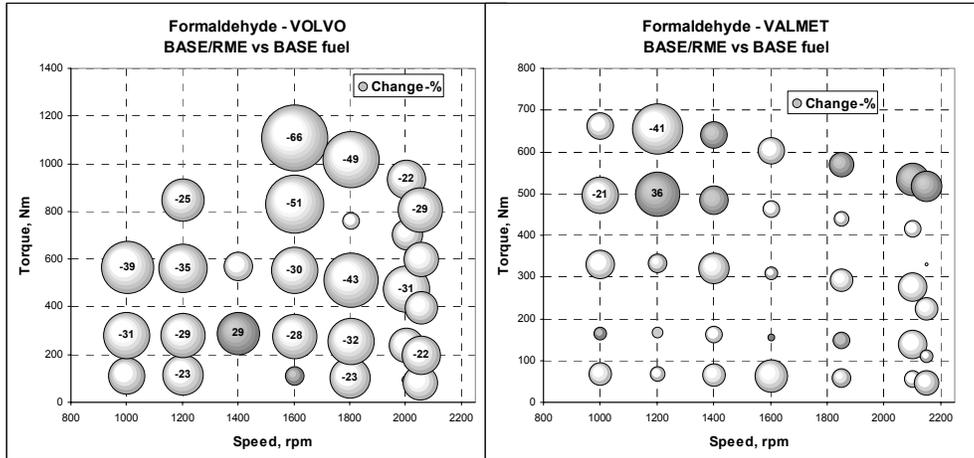*Figure 11. Formaldehyde emission (mg/kWh) for base fuel. Engine mapping tests with Volvo and Valmet engines.*

*Figure 12. Relative differences (%) in formaldehyde emission when RME blend is compared to BASE fuel. Light bubbles mean lower emissions for RME containing fuel. Only significant changes are shown as numbers.*

# 8    13-MODE TEST CYCLES

## 8.1    GENERAL

The major part of the heavy-duty tests were carried out according to the ECE R49 test procedure, which includes 13 load modes with various torque and speed combinations (Figure 13). The average values for the last 60 seconds in each 6-minute mode are used in the calculations of the final results of gaseous emissions.

The particulates are collected on one pair of filters during the test, and the weighting factors are taken into account by adjusting the collection time in each mode to correspond to the weighting factor of each load mode. The particulate sampling time is normally shorter than 6 minutes. In these measurements, the collection time of particulates was adjusted longer than normally to collect enough of particulate mass. This meant that the actual running time was longer than 6 minutes in mode 6, which has the highest weighting factor and thus also the longest sampling time.

The Japanese test cycle also includes 13 load modes with various torque and speed levels (Figure 14). However, the speed/load map is different from the European test cycle. The full load modes are decisive in the European test cycle, whereas lower speed/load conditions dominate the outcome in the Japanese test cycle. Each mode lasts from 2 to 5 minutes, and the measurement time depends on the weighting factor of the mode. The average values of each mode are used in the calculations of the final results of gaseous emissions. Particulates are collected on one pair of filters during the test, and the weighting factors are taken into account by adjusting the collection time in each mode to correspond to the weighting factor of each mode.
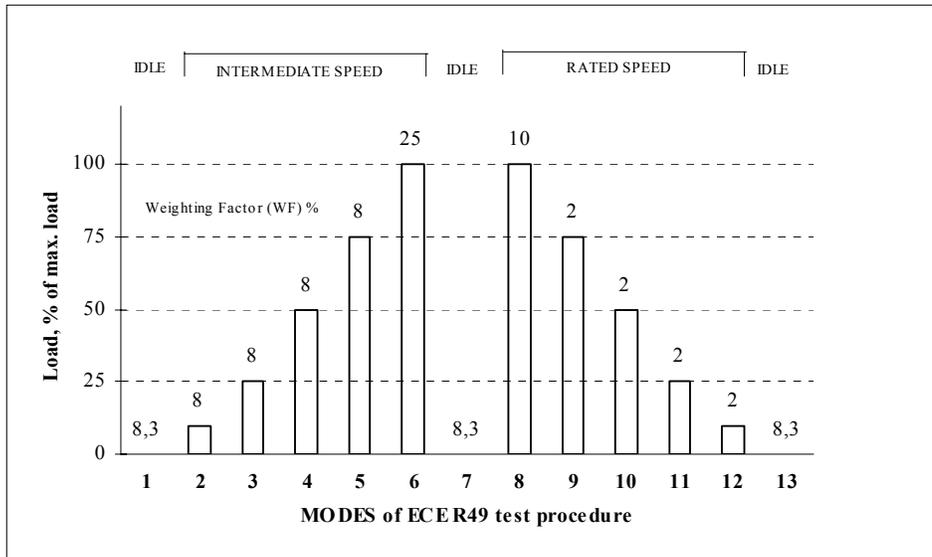
*Figure 13. The European 13-mode test procedure for HD engines, ECE R49.*
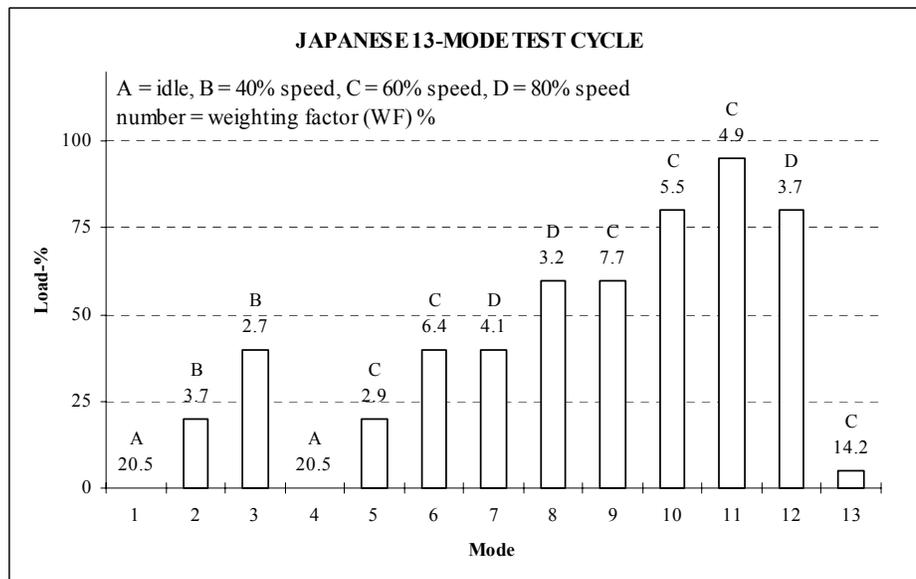


*Figure 14. The Japanese 13-mode test procedure for heavy-duty engines.*

The actual load points determined for the Volvo engine according to Japanese and European 13-mode test method are shown in Figure 15.

The injection pump of the diesel engine operates on a volumetric base. A low-density fuel produces less power that a high-density fuel, and this affects the emission level. When fuels are compared with each other, it is reasonable to use the same load settings of dynamometer for all fuels. In this study, the maximum power of 190 kW / 2000 $min^{-1}$ and the maximum torque of 1100 Nm/1450 $min^{-1}$

were used for all fuels except for the EtDI fuel. This fuel arrived late, and did not produce as high power output as the other fuels.
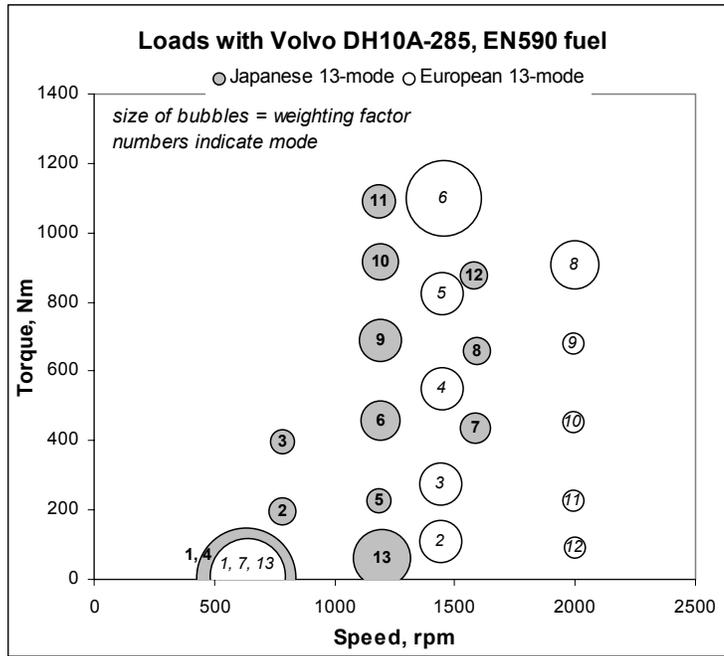


*Figure 15. The summary of loads and weighting factors of Japanese and European test cycles with Volvo engine.*

## 8.2   COMPARISON OF JAPANESE AND EUROPEAN TEST CYCLES

The results of the tests with the Japanese and European test cycles with two fuels (EN590 and RME30) are shown in Table 8. The relative differences in emissions when RME30 fuel is compared to EN590 fuel are shown in Figure 16.

HC and formaldehyde emissions were significantly higher with the Japanese test cycle than with the European test cycle. CO and $NO_x$ emissions were also slightly higher with the Japanese test cycle. No significant differences in PM emissions were seen between the two test cycles for the EN590 fuel. However, the Japanese test gave a higher PM result for the RME30 fuel than the European test cycle. RME is known to produce more wet particulates at idle than the hydrocarbon fuels do. The Japanese test cycle includes long periods of idling, and probably this is the reason why the particulate emission was higher for RME using the Japanese test cycle.

Regarding CO and $NO_x$ emissions the differences in emissions between the EN590 and the RME30 fuel seem to be similar with the Japanese and European test cycles. Contrary to this, the results obtained with the European test cycle for

HC, particulates and formaldehyde emissions are not in line with the results obtained with the Japanese test cycle, for reasons explained previously.

*Table 7. The emission results with Japanese and European 13-mode test for EN590 and RME30 fuels.*

|  | HC g/kWh | CO g/kWh | NOx g/kWh | PM g/kWh | CO2 g/kWh | Fuel cons. g/kWh | Formald. mg/kWh |
|---|---|---|---|---|---|---|---|
| **Japanese 13-mode test** |  |  |  |  |  |  |  |
| EN590 | 0.31 | 0.61 | 7.4 | 0.073 | 692 | 236 | 71 |
| RME30 | 0.25 | 0.58 | 7.5 | 0.080 | 690 | 245 | 70 |
| **European 13-mode test** |  |  |  |  |  |  |  |
| EN590 | 0.17 | 0.53 | 5.9 | 0.075 | 695 | 232 | 31 |
| RME30 | 0.17 | 0.48 | 6.0 | 0.057 | 686 | 240 | 21 |
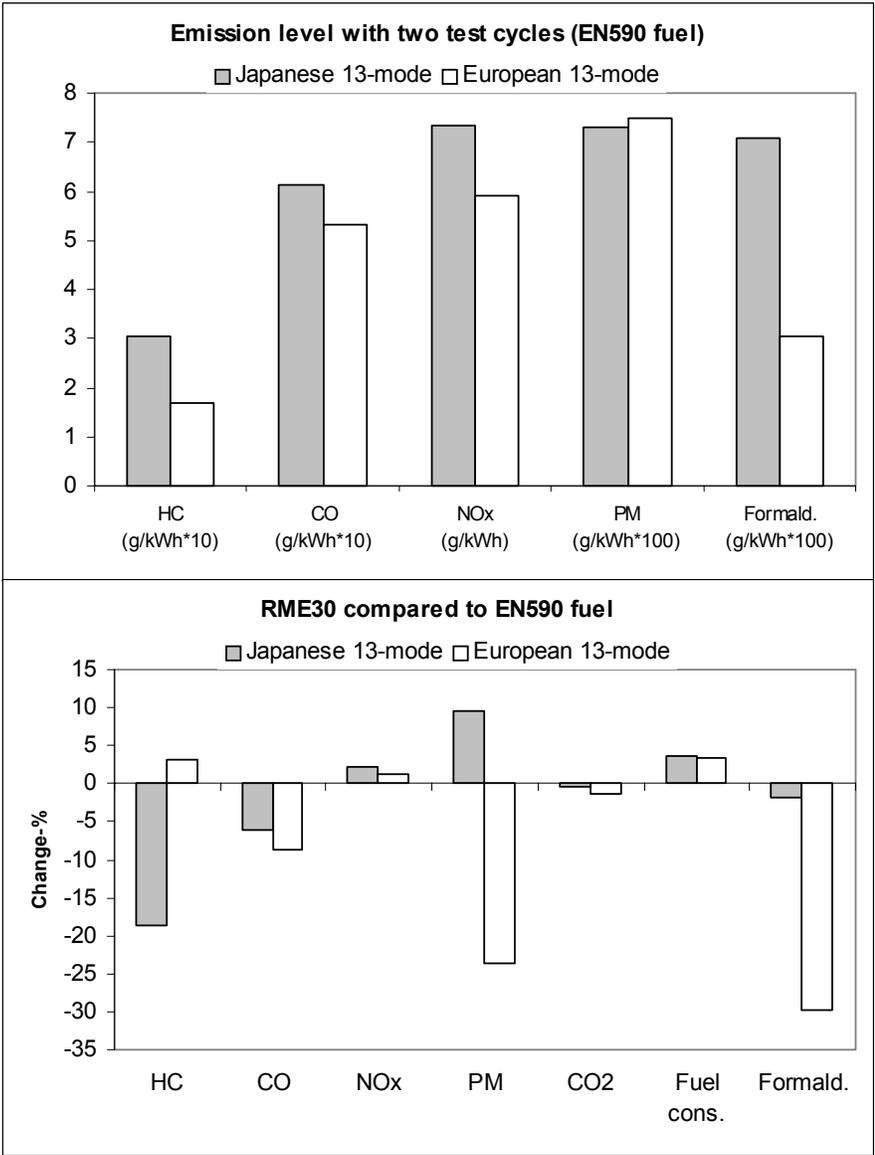


*Figure 8. Emission results with the Japanese and European test cycle and differences (%) when RME30 fuel is compared to EN590 fuel.*

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# 9 RESULTS WITH HD VOLVO ENGINE

## 9.1 STABILITY OF THE VOLVO ENGINE

The tests with the Volvo DH10A-285 engine were carried out without a catalyst, with an oxidation catalyst and with a CRT catalyst/trap. The tests were divided into two testing periods. The tests without and with an oxidation catalyst were run in one period at the beginning of the project, and the tests with the CRT in the second period almost one year later. The stability of the Volvo engine was checked by running the engine without catalyst before and after both periods. The diesel fuel used for the stability checks was Finnish wintergrade low-emission fuel, and test cycle used was ECE R49. It was observed that the $NO_x$ and particulate matter emissions had changed significantly in between the testing periods, while the CO and HC emissions remained more or less constant. The particulate matter emission was around 0.08 g/kWh at the beginning of the tests, and around 0.07 g/kWh during the the CRT tests. The $NO_x$ emission level increased from 5.4 g/kWh to 5.9 g/kWh, respectively (Figure 17).

The change in engine performance did not disturb the comparison of different fuel qualities, because the emission level was stable within each testing period. The only parameter that cannot be analysed due to the change in engine performance is the effect of the CRT device on $NO_x$ emissions. The 0.5 g/kWh change in the $NO_x$ level of the engine is higher than the effect of the aftertreatment devices studied. The possible $NO_x$ effect of the aftertreatment devices is most probably due to increased exhaust back-pressure and therefore increased internal EGR.
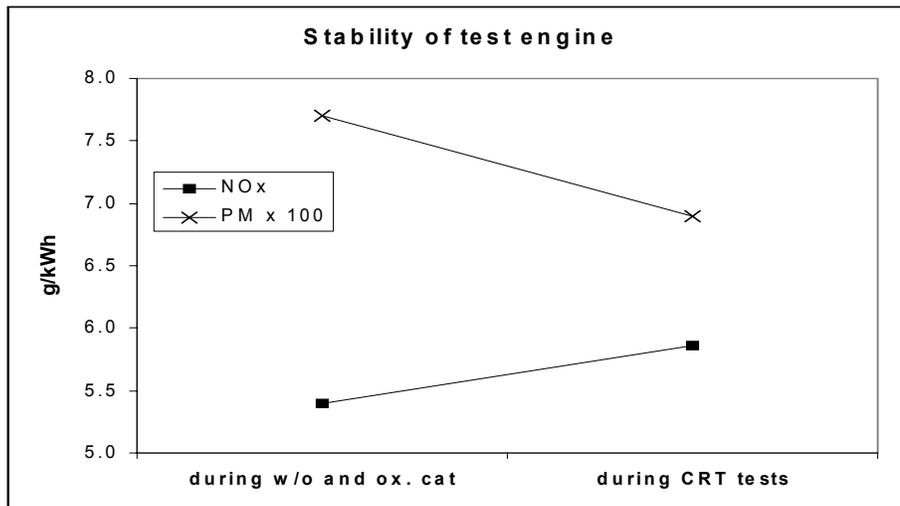


*Figure 9. The $NO_x$ and PM emission level of Volvo engine changed significantly between the two test periods.*

## 9.2 GASEOUS EMISSIONS

### 9.2.1 HC and CO emissions

The results of the regulated emissions of the Volvo engine according to the ECE R49 cycle are given in Appendix 5.

The HC emission levels of all fuels with the exception of EtDI were below 0.25 g/kWh in the tests without a catalyst (Figure 18). The HC emissions were low when compared to the limit value of the Euro 2 emission regulation (1.1 g/kWh). The oxidation catalyst reduced HC emissions by 70 - 80%. The CRT device was even more effective, the reductions in HC emissions were 94 - 99%. Actually, the HC concentrations in raw exhaust after the aftertreatment devices were generally below the detection limit of the analysis equipment. Especially with the CRT catalyst/trap the measured values were mostly close to zero level.

HC emissions with neat vegetable oil esters were lower than with the hydrocarbon base fuels both in the tests without a catalyst and with an oxidation catalyst. Adding 30% ester to diesel did not significantly affect the HC emission, even though two examples on reductions were seen (SME30 vs EN590 and RFD/RME30 vs RFD in the tests without catalyst). The HC emission was slightly higher with the fuel containing hydrated tall oil than with the EN590 fuel. However, the reason for this is most probably the quality of Canadian diesel fuel into which TO was blended. The EtDI fuel gave three times higher HC emission level than the EN590 fuel. However, the HC emission level with the EtDI fuel was still about one half of the Euro 2 limit value.

It was not relevant to analyse the differences between the test fuels regarding HC emissions in the tests with the CRT catalyst/trap due to the close-to zero level HC emissions.
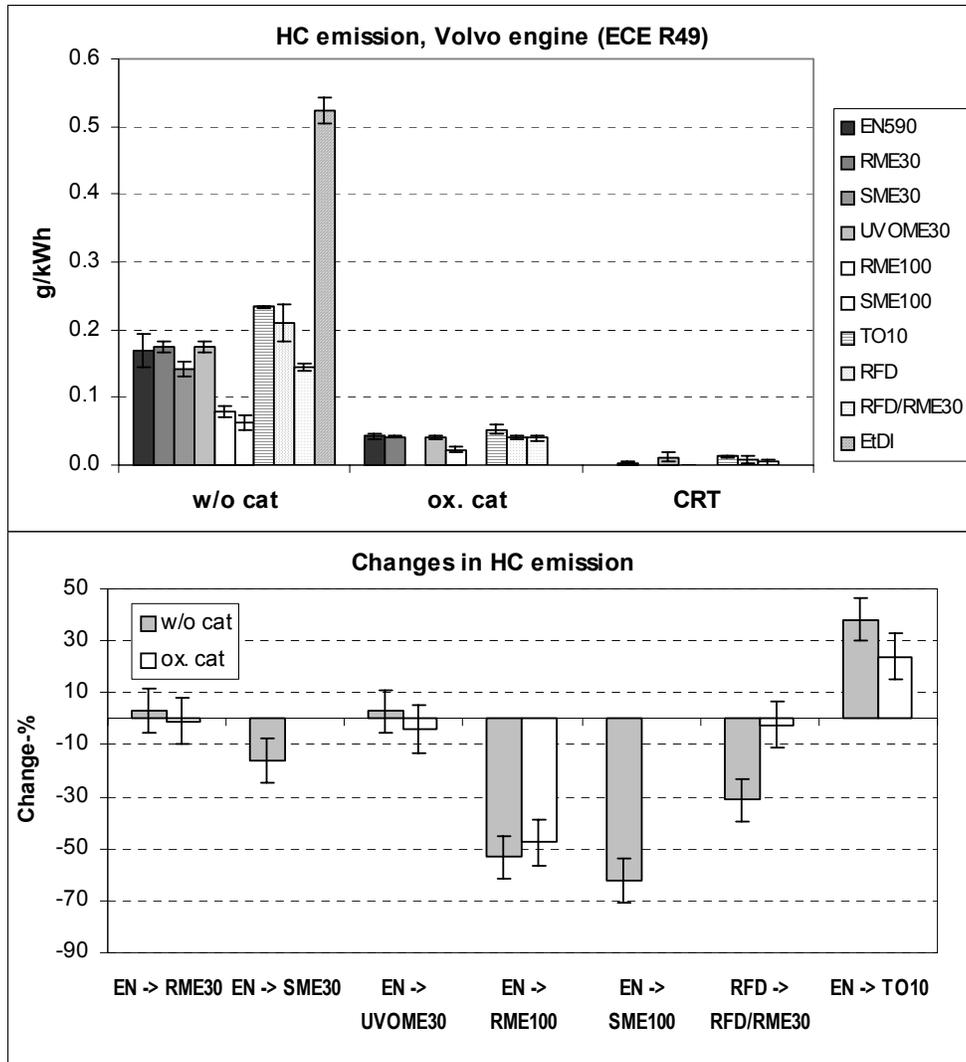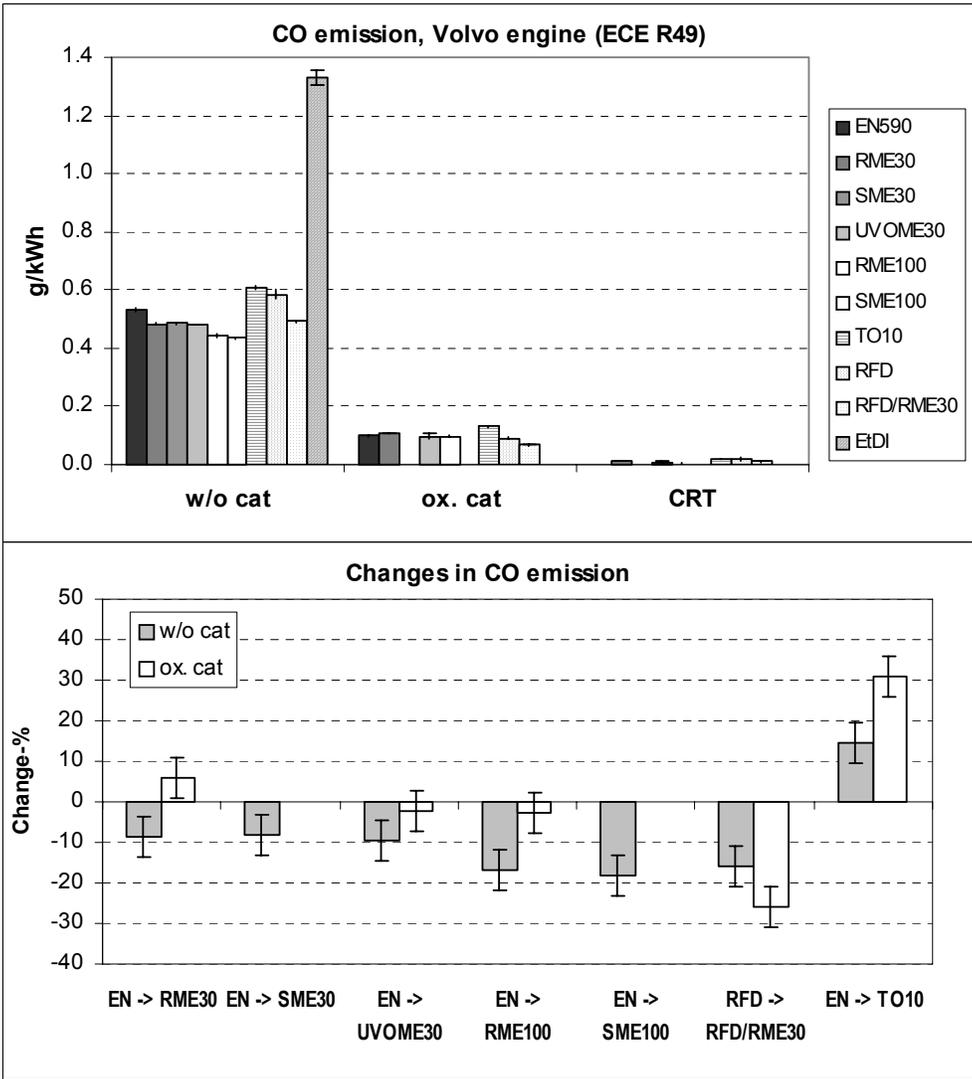
*Figure 18. HC emission with Volvo engine and the differences between the test fuels, ECE R49 test. Error bars represent absolute deviation for mass emission results and general deviation for relative differences.*

The CO emission level of the Volvo engine without a catalyst was below 0.6 g/kWh with all fuels except for the EtDI fuel. This fuel increased the CO emission by a factor of 2.5 compared to the EN590 fuel (Figure 19). However, even with the EtDI fuel the CO emission was very low compared to the Euro 2 limit value (1.3 vs. 4.0 g/kWh). The oxidation catalyst reduced CO emissions by about 80% and the CRT catalyst/trap by 97 - 99%. The CO concentrations with the CRT catalyst were below the detection limit at many load points.

In the tests without a catalyst the CO emission level was lower with the fuels containing biodiesel components than with the hydrocarbon fuels. RME tended to reduce CO emissions more when blended into RFD than into EN590. RME100 and SME100 fuels resulted in the lowest CO emissions in the tests without a

catalyst. The TO10 fuel gave slightly higher CO results than the EN590 fuel, and the EtDI fuel resulted in the highest CO emission.

In the tests with an oxidation catalyst the differences in CO emissions between the bioesters and EN590 fuel were not very significant. However, when 30% RME was blended into RFD, the CO emission decreased by more than 20% with the oxidation catalyst.

The CO emission levels with the CRT were too low to draw any conclusions from possible fuel effects.



*Figure 19. CO emission with Volvo engine and the differences between the test fuels, ECE R49 test. Error bars represent absolute deviation for mass emission results and general deviation for relative differences.*

### 9.2.2   $NO_x$ emission

The $NO_x$ emission level ranged 5 - 7 g/kWh depending on the fuel. Again the EtDI was an execption; with EtDI the $NO_x$ emission level was below 5 g/kWh (Figure 20). In general, the $NO_x$ emissions were rather close to the Euro 2 limit value of 7 g/kWh.

Different aftertreatment alternatives (w/o cat, with oxidation cat and with CRT) were tested during two testing periods. It was observed that the $NO_x$ emission level of the engine increased significantly in between the testing periods as described in chapter 9.1. Hence, it is not possible to study the effect of the CRT device on $NO_x$ emissions. This does not, however, obscure the comparison of the different test fuels, because the fuel matrixes were run within a short time period with each aftertreatment alternative.

In the tests without a catalyst and with an oxidation catalyst the change in $NO_x$ emissions with fuels containing 30% ester compared to EN590 fuel was surprisingly small – negligible when standard deviation is taken into account. The addition of 30% RME into the RFD fuel resulted in an increase in $NO_x$ emission of almost 8%. The RME100 and SME100 fuels resulted in a some 13% higher $NO_x$ emission level than the EN590 base fuel. The fuel containing hydrated tall oil and EtDI fuel reduced the $NO_x$ emission.

The EN590 fuel was not tested with the CRT (too high sulfur content). Thus the same kind of comparison regarding $NO_x$ emissions could not be done as for the other tests. However, it was seen that adding 30% of RME in the RFD fuel resulted in a 7% increase in the $NO_x$ emission when running the engine with the CRT device.

When the individual modes of the ECE R49 test (w/o catalyst) are considered, it can be noted that the effect of adding 30% bioester into the EN590 fuel was negligible on the $NO_x$ emissions in all load conditions (Figure 21). Even though the changes generally were insignificant, the trend seems to be that adding 30% bioester into the EN590 fuel slightly increases the $NO_x$ emission at modes with 25% or higher load (Modes 3, 4, 5, 6, 9, 10, 11). The differences are negligible or even inverse on 10% load and also on 100% load at rated speed (modes 2, 8 and 12). A similar result was obtained in the engine mapping tests. When 30% RME was added to the RFD fuel, the $NO_x$ emission levels clearly increased at load levels of 25% or higher (other than Modes 2 and 12). The same applies when neat bioesters are compared to the EN590 fuel. The EtDI fuel clearly reduced $NO_x$ emissions when compared to the EN590 fuel in all other load conditions than on 10% and 25% loads with intermediate speed (Modes 2 and 3).
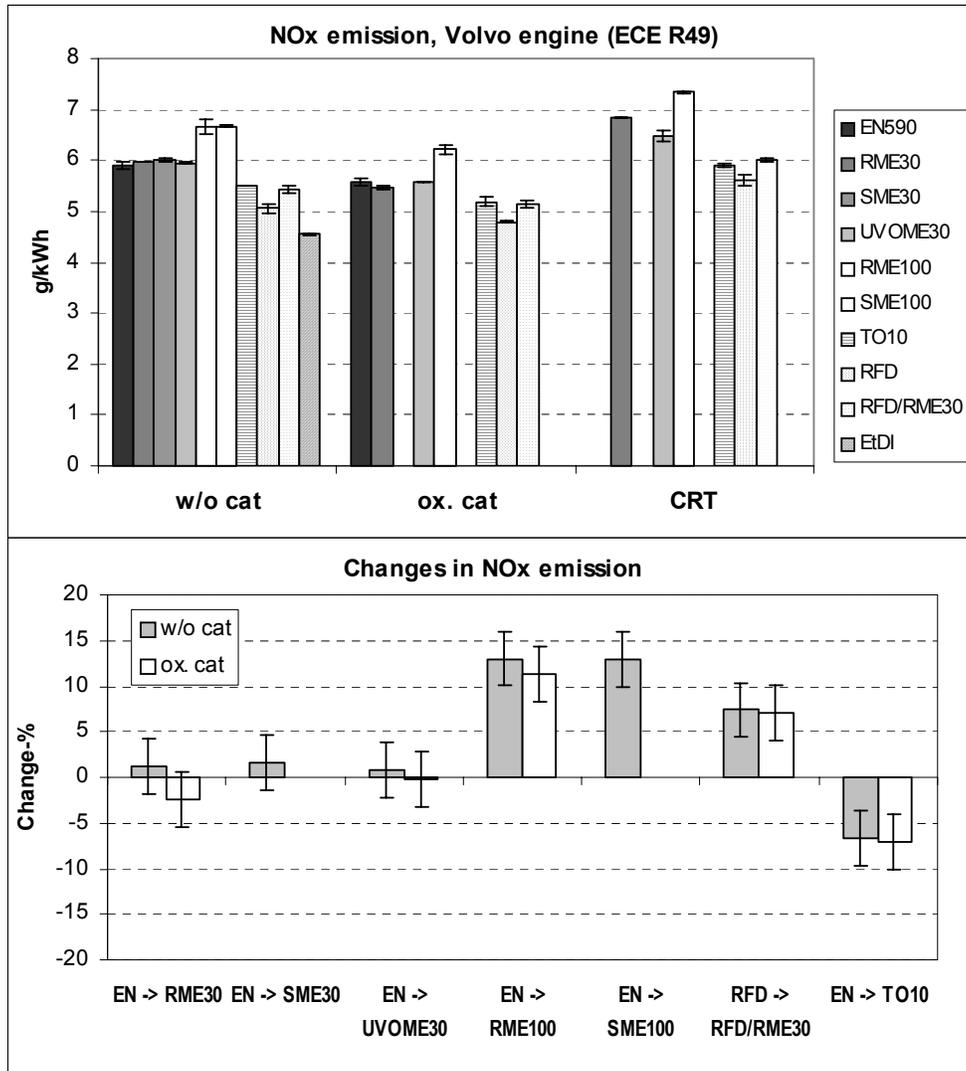
*Figure 20. NO$_x$ emission with Volvo engine and the differences between the test fuels, ECE R49 test. Error bars represent absolute deviation for mass emission results and general deviation for relative differences.*
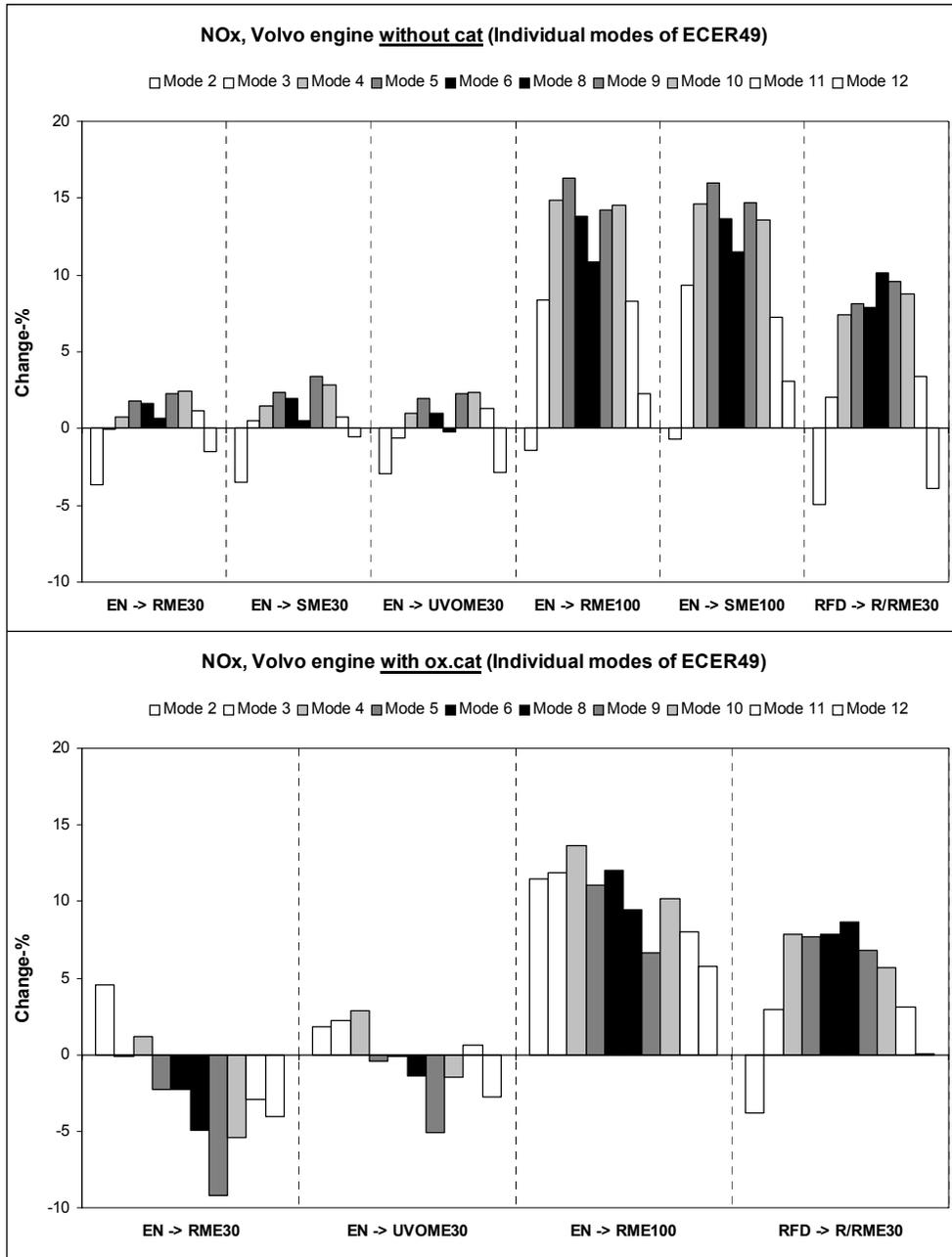
*Figure 10. The differences between test fuels for NO$_x$ emission in individual loaded modes of ECE R49 test, Volvo engine without and with aftertreatment devices.*

### 9.2.3 Formaldehyde and other FTIR results

The FTIR results of selected compounds are shown in Appendix 6. The concentrations of many compounds that can be analysed with the FTIR equipment are below the detection limit in the exhaust gas from diesel engines. Hence, the

main interest of the FTIR results with diesel engines is in the formaldehyde emission.

The formaldehyde emissions are reduced with aftertreatment devices (Figure 22). The oxidation catalyst reduced formaldehyde emission by 15 - 40%, with the exception of the RME30 fuel. CRT was much more efficient in reducing formaldehyde emissions than the oxidation catalyst. The reduction in formaldehyde emissions with CRT ranged 65 - 95%.

The fuel impact on formaldehyde emissions could not be analysed reliably in the tests with aftertreatment devices due to the low emission levels. In the tests without a catalyst, the EtDI fuel resulted in the highest formaldehyde emission levels. RME seemed to reduce formaldehyde emission as a blend, but not as neat RME (RME100) and not when compared to reformulated base fuel. TO10 gave slightly higher formaldehyde emission levels than the EN590 fuel. The other fuels did not affect formaldehyde emissions significantly.
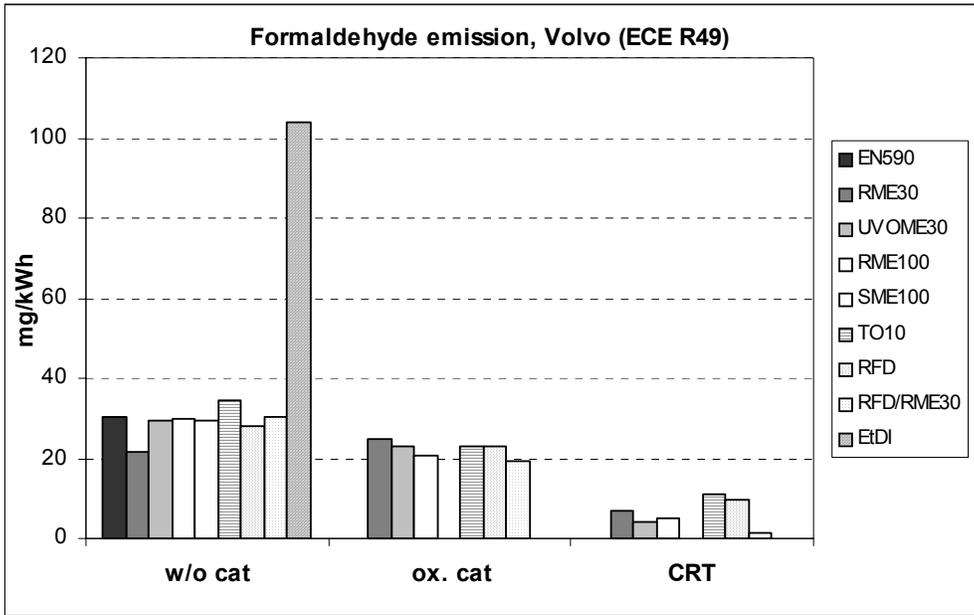


*Figure 22. Formaldehyde emission with Volvo engine, ECE R49 test.*

The $NO_2$ formation with the aftertreatment devices was high compared to the results without catalyst. $NO_2$ emissions were more than two times higher with the oxidation catalyst and even 9 times higher with the CRT device than without catalyst. There were great differences in $NO_2$ formation from test to test, but the differences seemed not to be fuel-related. Most probably the $NO_2$ emission levels varied due to random changes in the operation of the aftertreatment devices.

Strong $NO_2$ formation, especially with the CRT catalyst, results in an unpleasant odour, which can be detected easily on the road. Eventually, most tailpipe NO soon converts to $NO_2$ in ambient air.

The formation of laughing gas ($N_2O$) and ammonium ($NH_3$) were below the detection limits of FTIR in all tests – almost at zero level.

The only hydrocarbon compound that exceeded the detection limit with FTIR was n-octane.

## 9.3    TOTAL PARTICULATES AND BLACK SMOKE

The particulate matter emission of the Volvo engine was below 0.09 g/kWh in the tests without a catalyst (Figure 23). This is clearly lower than the Euro 2 limit value of 0.15 g/kWh.

The oxidation catalyst used in these tests was planned to tolerate sulfur contents of up to 500 ppm. Hence, the particulate emission level of the Volvo engine stayed below the Euro 2 limit value also with the fuels generating sulfates with the oxidation catalyst. However, the oxidation catalyst clearly increased particulate emissions compared to the base case without catalyst for the fuels containing 300 - 400 ppm of sulfur. Oxidation catalyst slightly reduced the particulate emission for the RME100 fuel, but not for the other fuels with very low sulfur content (RFD and RFD/RME30).

Particulate matter emissions were 10 - 50% lower for the fuels containing 30% ester than for the base fuels both in the tests without a catalyst and with an oxidation catalyst (Figure 23). The reduction of the particulate matter emission with RME100 and SME100 was huge (60 - 80%) compared to the EN590 fuel. TO10 resulted in a higher particulate matter emission than the EN590 fuel in the tests without catalyst, but in lower emissions in the tests with the oxidation catalyst. The EtDI fuel gave a lower particulate matter emissions than the EN590 fuel.

The CRT catalyst/trap reduced particulate matter emissions effectively (73 - 87 %) with fuels RME100, RFD and RFD/RME30. The absolute emission level with these fuels was around 0.01 g/kWh, which is a hardly measurable emission level (below 0.5 mg particulate mass on the filter paper). No significant reduction in the particulate matter emission was seen with the CRT for the TO10 fuel. This could be explained by a trace effect from higher-sulfur fuels that were run before the TO10 fuel, even though a low-sulfur fuel was run in between to stabilize the CRT. The particulate matter results for fuels RME30 and UVOME30 are not dicussed as the sulfur level of the fuels was higher than recommended by the manufacturer of the CRT.

Black smoke values were significantly lower for the ester-containing fuels than for the base fuels (Figure 24). The TO10 fuel resulted in rather high particulate matter emissions and black smoke values, near to the values of the EN590 fuel.
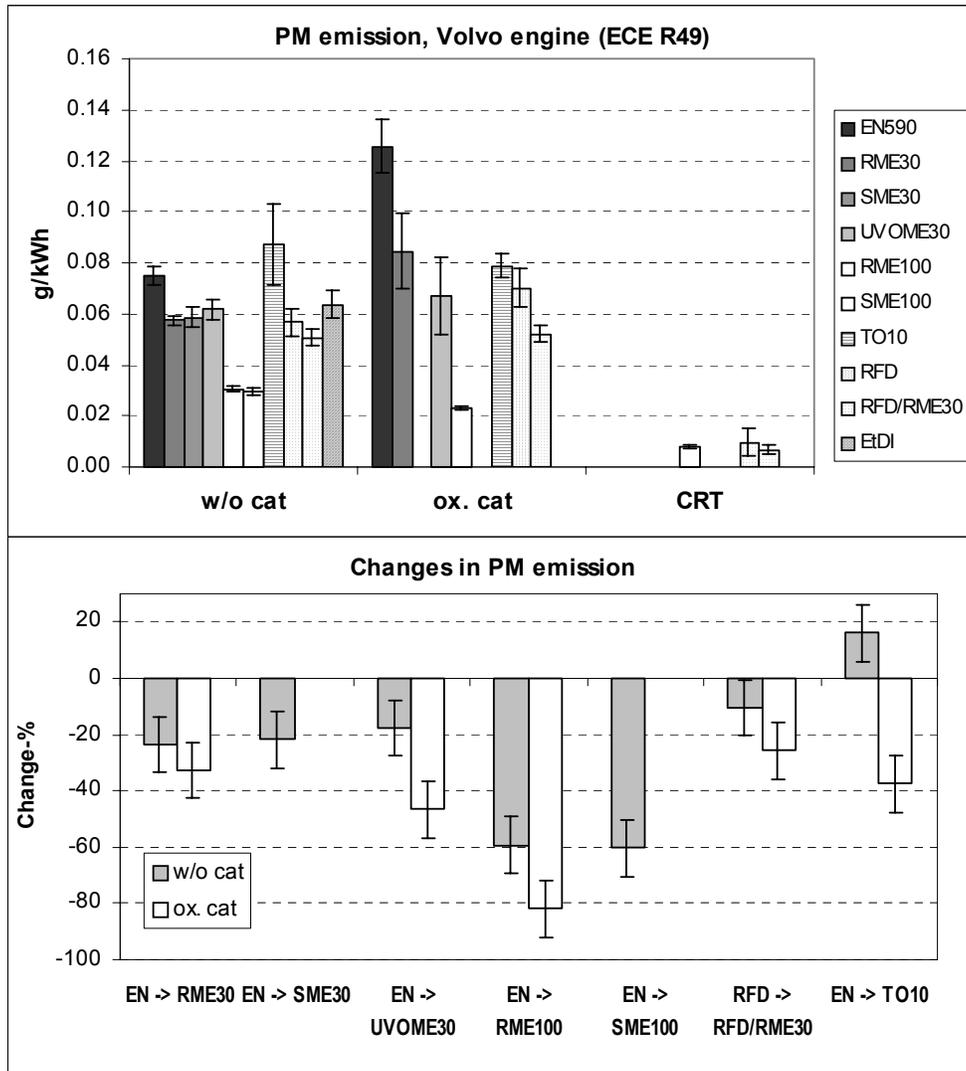
*Figure 23. PM emission with Volvo engine and the differences between the test fuels, ECE R49 test. Error bars represent absolute deviation for mass emission results and general deviation for relative differences.*
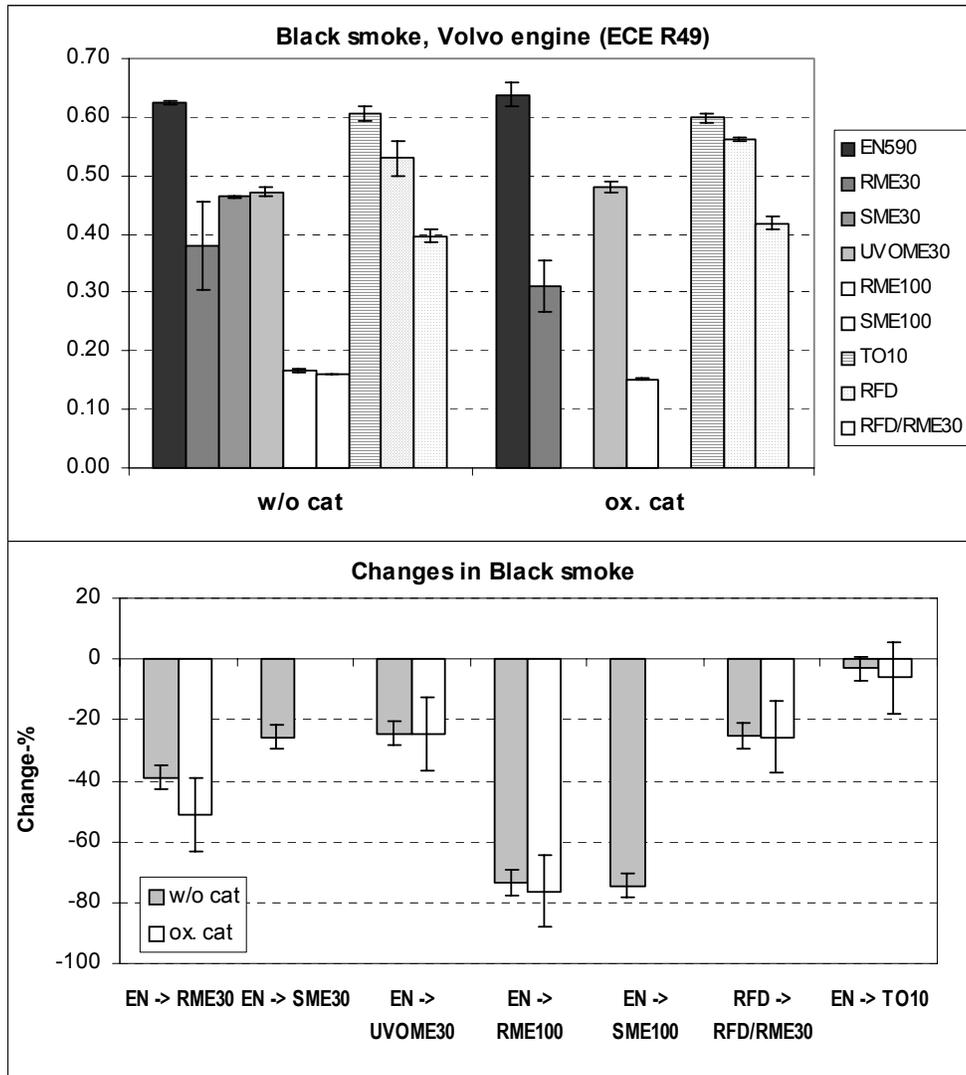
*Figure 24. Black smoke with Volvo engine and the differences between the test fuels, ECE R49 test. Error bars represent absolute deviation for mass emission results and general deviation for relative differences.*

## 9.4    COMPOSITION OF PARTICULATES

The compositional analysis of particulates included determination of the soluble organic fraction (SOF) and sulfates. The SOF portion represents organic compounds, which can be extracted with dichloromethane. The remaining portion (others than SOF or sulfates) mainly consists of elementary carbon, but also of e.g. metals and nitrates. However, to simplify the discussion, hereinafter this portion is called "black carbon". The numerical results of the compositional particulate analyses are given in Appendix 7.

*In the tests without catalyst* the major part of the particulate mass was "black carbon" (Figures 25 - 27). This portion reduced clearly as the biocomponent content of fuel increased (Figure 25). The SOF mass emission did not change as drastically as the "black carbon" portion when switching from fuel to another. As a result, the relative SOF fraction clearly increased as the biocomponent content of fuel increased. The relative SOF fraction of particulates was 10 - 15% with EN590 and RFD fuels, 20 - 30 % with blended biofuels and 40 - 50% with neat biofuels RME100 and SME100. The share of sulfates and combined water was 10 - 15% with sulfur-containing fuels. Particulates did not contain any significant amount of sulfates with very low sulfur level fuels (RME100, SME100, RFD and RFD/RME30).

*The oxidation catalyst* did not affect significantly the "black carbon" portion of the particulates with the EN590 and RFD fuels, whereas for the biofuels this portion was lower with the catalyst than without it. The oxidation catalyst reduced the SOF emission for all fuels except the RFD fuel. However, the particulates with the biofuels were still after the oxidation catalyst generally more wet than with the EN590 fuel (Figure 28). On the other hand, the deviation of the SOF results was rather high in the tests with oxidation catalyst.

The oxidation catalyst stronly promoted sulfate formation: sulfates and combined water represented 20 - 60% of the particulate matter. However, all particulate results were still below the Euro 2 limit value. Sulfates and combined water with the RFD fuel were close to the theoretical output calculated from 10 ppm of sulfur in the fuel. As the actual sulfur level of the RFD fuel was lower than 10 ppm, it seems that lubricating oil played a role in sulfate formation.

Altogether, if the oxidation catalyst and neat biofuels were combined, very low particulate matter emissions were obtained. Primarily this was a result of the low "black carbon" portion of particulates for the bioesters, the effect of the oxidation catalyst on the SOF fraction was less important.

The CRT device generated sulfates formation as effectively as the oxidation catalyst in relative terms (Figure 29). The high SOF fraction for the RME100 fuel was also seen clearly. However, the absolute particulate emissions for the fuels with less than 50 ppm sulfur with the CRT were really low. Thus the absolute emissions of sulfates, SOF and others were only a fraction of that obtained in the tests without catalyst and with oxidation catalyst.
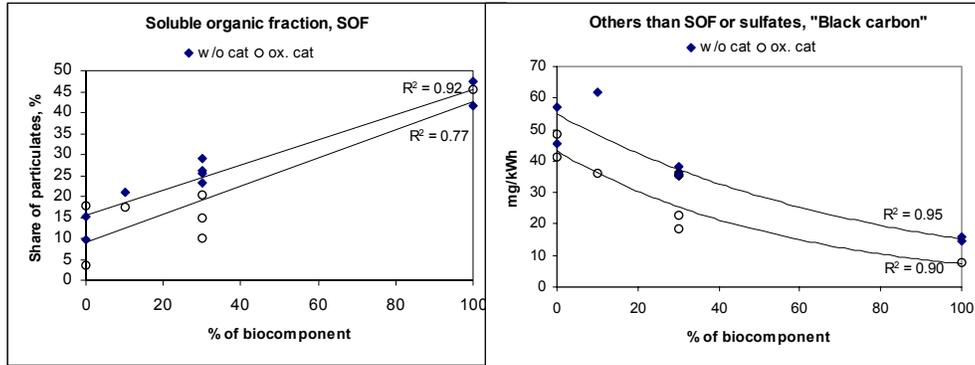
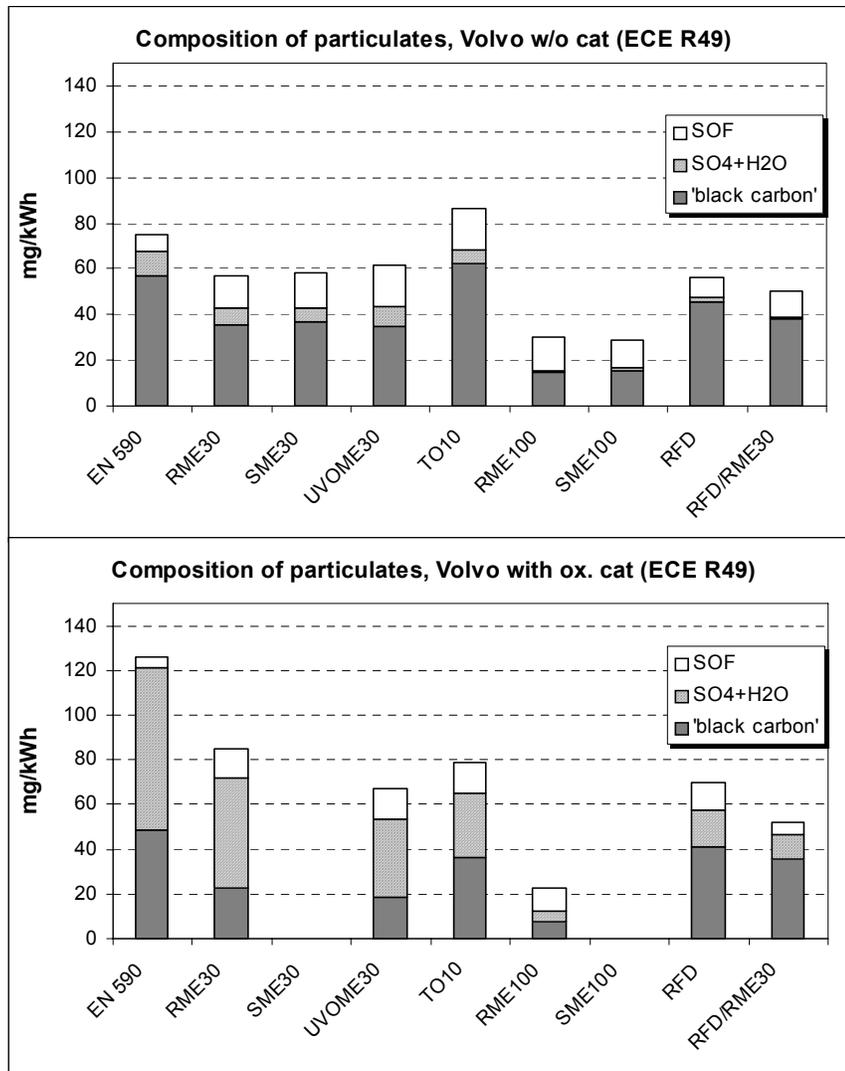*Figure 25. SOF and others than SOF or sulfates vs biocomponent content of fuels.*



*Figure 26. Composition of particulates as mg/kWh with Volvo engine without catalyst and with oxidation catalyst, ECE R49 test.*
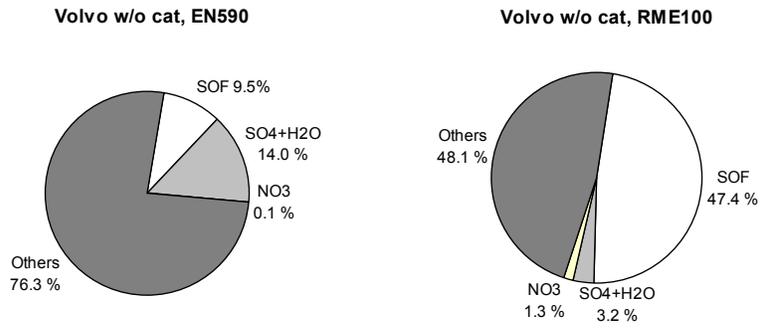
**Volvo w/o cat, EN590**

SOF 9.5%

SO4+H2O
14.0 %

NO3
0.1 %

Others
76.3 %

**Volvo w/o cat, RME100**

Others
48.1 %

SOF
47.4 %

NO3
1.3 %

SO4+H2O
3.2 %

*Figure 27. Composition of particulates as percentages with Volvo engine without catalyst, ECE R49 test.*

**Volvo ox. cat, EN590**

SOF 9.5%

Others
38.6 %

NO3
0.0 %

SO4+H2O
57.8 %
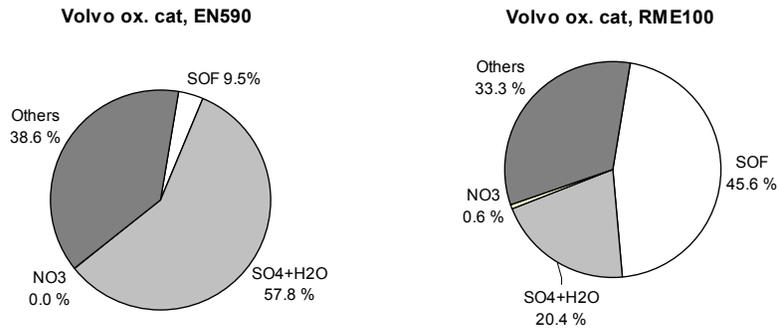
**Volvo ox. cat, RME100**

Others
33.3 %

SOF
45.6 %

NO3
0.6 %

SO4+H2O
20.4 %

*Figure 28. Composition of particulates as percentages with Volvo engine with oxidation catalyst, ECE R49 test.*

**Volvo with CRT, RME100**

NO3
0.0 %

Others
9.4 %

SO4+H2O
27.4 %

SOF
63.2%

**Volvo with CRT, RFD/RME30**

NO3
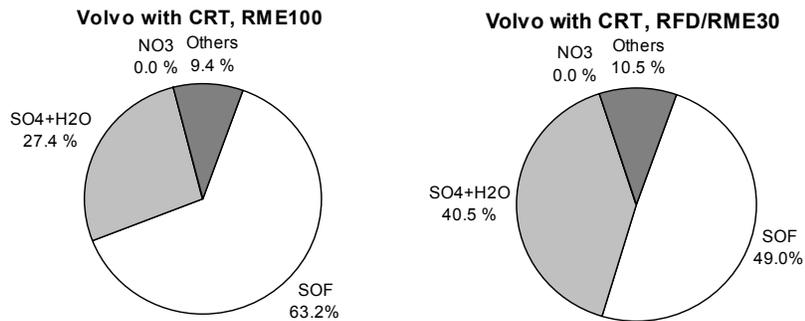0.0 %

Others
10.5 %

SO4+H2O
40.5 %

SOF
49.0%

*Figure 29. Composition of particulates as percentages with Volvo engine with CRT catalyst, ECE R49 test.*

## 9.5 PAH COMPOUNDS IN PARTICULATE AND SEMIVOLATILE PHASE

The numerical results of the PAH analyses are presented in Appendix 8.

The major part of the PAHs was found in the semivolatile phase. The semivolatile phase PAHs were determining both in the tests without and with catalysts. The major part of the semivolatile phase PAHs were light PAHs, whereas heavier PAHs were found in the particulate phase.

The general reduction of 14 PAHs in particulate and semivolatile phases was more than 60% with the oxidation catalyst for the major part of the fuels (Figure 30). However, with some fuels (RME100, RFD and RFD/RME30) the effect of catalyst seemed not to be really significant.

The level of PAH compounds in the particulates hardly exceeded the detection limit with the CRT catalyst/trap. The level of PAH compounds in the semivolatile phase was roughly the same with oxidation catalyst and CRT.

The differences between the test fuels were difficult to analyse due to the low PAH emission level of this engine. Figure 31 shows the differences between the test fuels and the deviation of the measurements in the tests without catalyst. It seems that the bioesters reduced the PAH emission level with the Volvo engine when no aftertreatment was used. In the tests without catalyst all fuels containing bioesters resulted in lower particulate and semivolatile phase PAH emissions than the EN590 fuel. The most clear benefit was seen for the RME100 and SME100 fuels. The differences for the ester blends were close to the deviation of the measurement method. When 30% RME was added to the RFD fuel, only a little benefit was seen regarding the PAH emission. The RFD fuel resulted in a rather high particulate PAH levels, almost the same as that for the EN590 fuel in the tests without catalyst. On the other hand, the PAHs were on a very low level in the semivolatile phase with the RFD fuel. No real benefit in PAH emissions were seen for the EtDI or TO10 fuels compared to the EN590 fuel. Those fuels resulted in the highest PAH levels in the particulate phase, but not in the semivolatile phase.

In the tests with catalysts the PAH emission levels were so low that in most cases the differences between the fuels were within deviation. It seemed that RME might reduce the level of 14 PAHs in the particulate SOF, but the high PAH result with RDF is very doubtful.
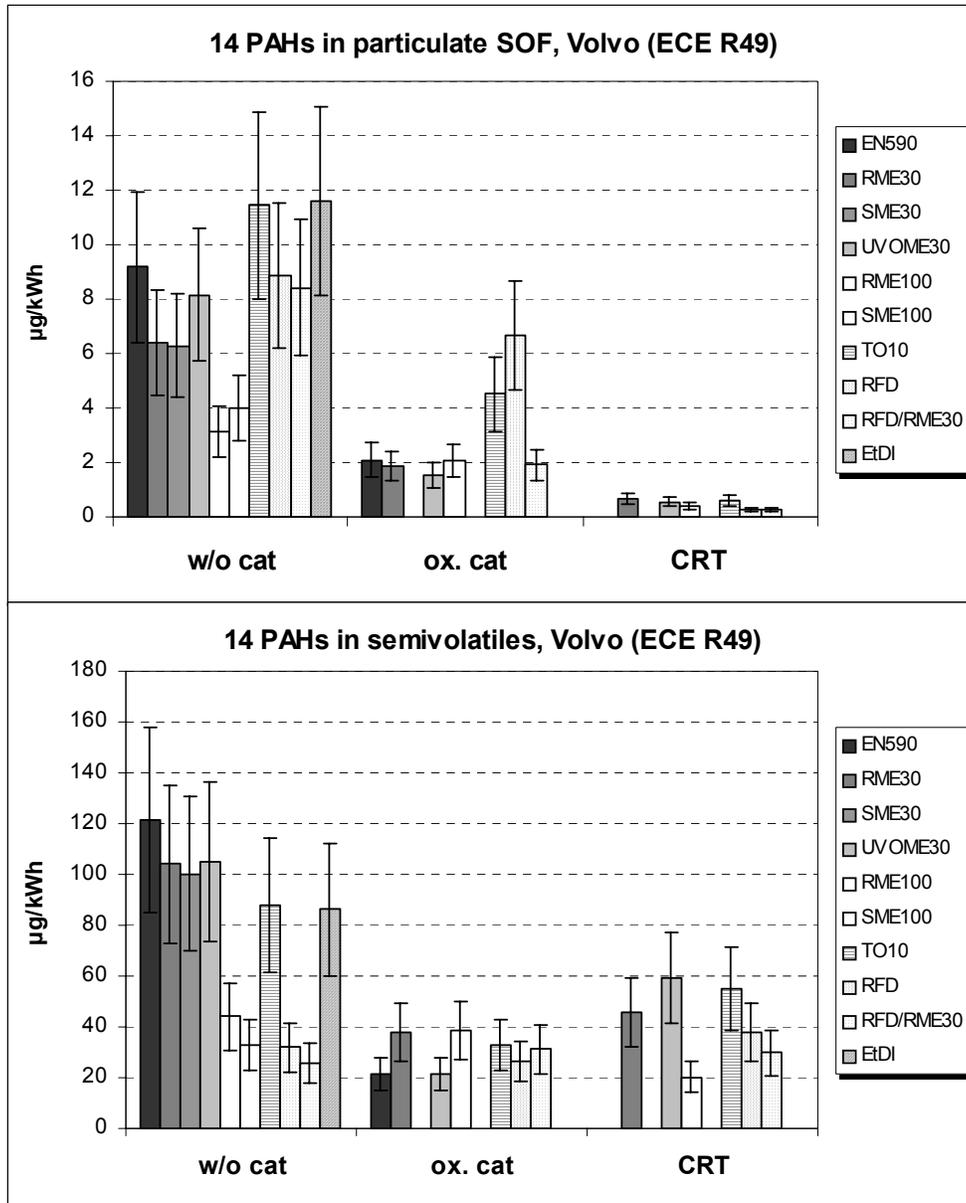
*Figure 30. Sum of 14 PAH compounds in particulate matter and semivolatile phase with Volvo engine, ECE R49 test.*
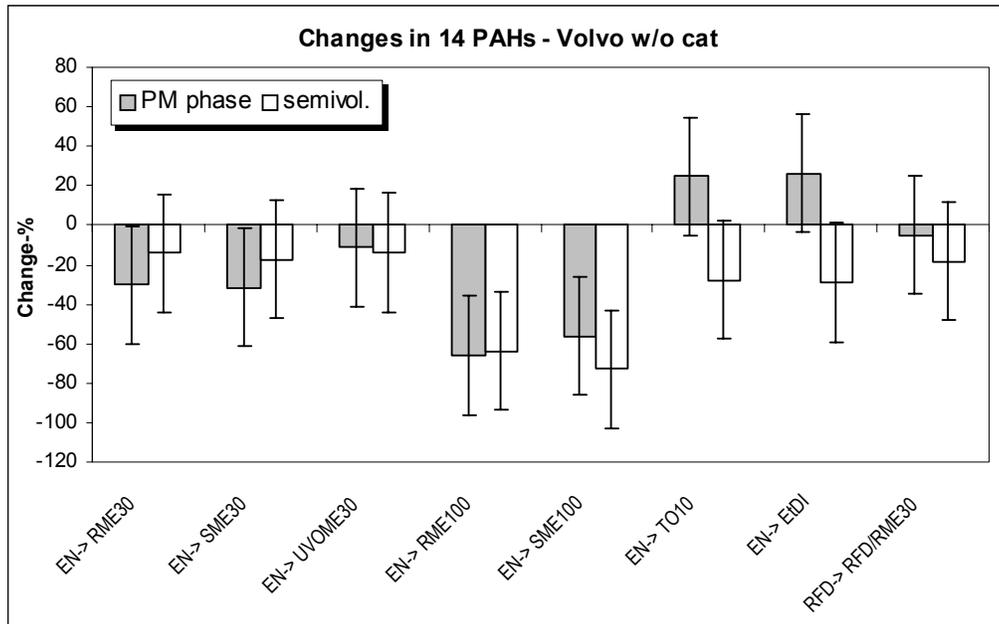
*Figure 31. The effect of fuel on the sum of 14 PAHs with Volvo engine, ECE R49.*

## 9.6    AMES TEST RESULTS

The results of the Ames test on the particulate SOF fraction are shown in Appendix 9 and graphically in Figure 32.

The Ames tests were carried out with two bacteria strains. Strain TA98-S9 was selected, because it has shown good response on diesel particulates in previous work carried out at VTT. The other strain, TA98NR-S9, was selected to study the effect of nitrated PAH compounds on mutagenicity. The results with strain TA98NR-S9 were low compared to those with TA98-S9 for all test fuels with and without oxidation catalyst. This indicates that nitrated PAH compounds have a significant effect on mutagenicity with diesel fuels and with bioesters. The masses of the samples collected in the CRT tests were not high enough to study mutagenicity with both bacteria strains.

The oxidation catalyst reduced the mutagenic activity of the particulate SOF fraction efficiently with the exception of RFD and RFD/RME30, which already had very low mutagenic activity without catalyst. The oxidation catalyst reduced the mutagenicity levels to one third of those without catalyst for all fuels other than RFD and its blend.

The Ames results with the CRT device were relevant only for fuels with a sulfur level lower than 50 ppm (RME100, RFD, TO10). No significant changes in mutagenic activity were observed when the results without catalyst were compared with those with CRT (for RME100 and RFD fuels), even though the mass particulate emission reduced dramatically with the CRT device. It can be

assumed that nitrated PAH compounds may be the reason for the unexpectedly high mutagenic activity with the CRT catalyst/trap.

Adding 30% of bioester to the base fuel or switching the EN590 fuel to EtDI did not result in any significant effect on the mutagenic activity of the particulate SOF fraction, considering the uncertainty of the measurement method. Neat bioesters generally showed a lower mutagenic activity than the EN590 or the biodiesel blends. The RFD and RDF/RME30 fuels resulted in the lowest mutagenic activity in the tests without catalyst (even lower than RME100 and SME100). The TO10 fuel showed a rather high mutagenic activity in the tests without catalyst, but a low activity in the tests with catalyst, which is suspected to indicate the discrepancy of the samples.
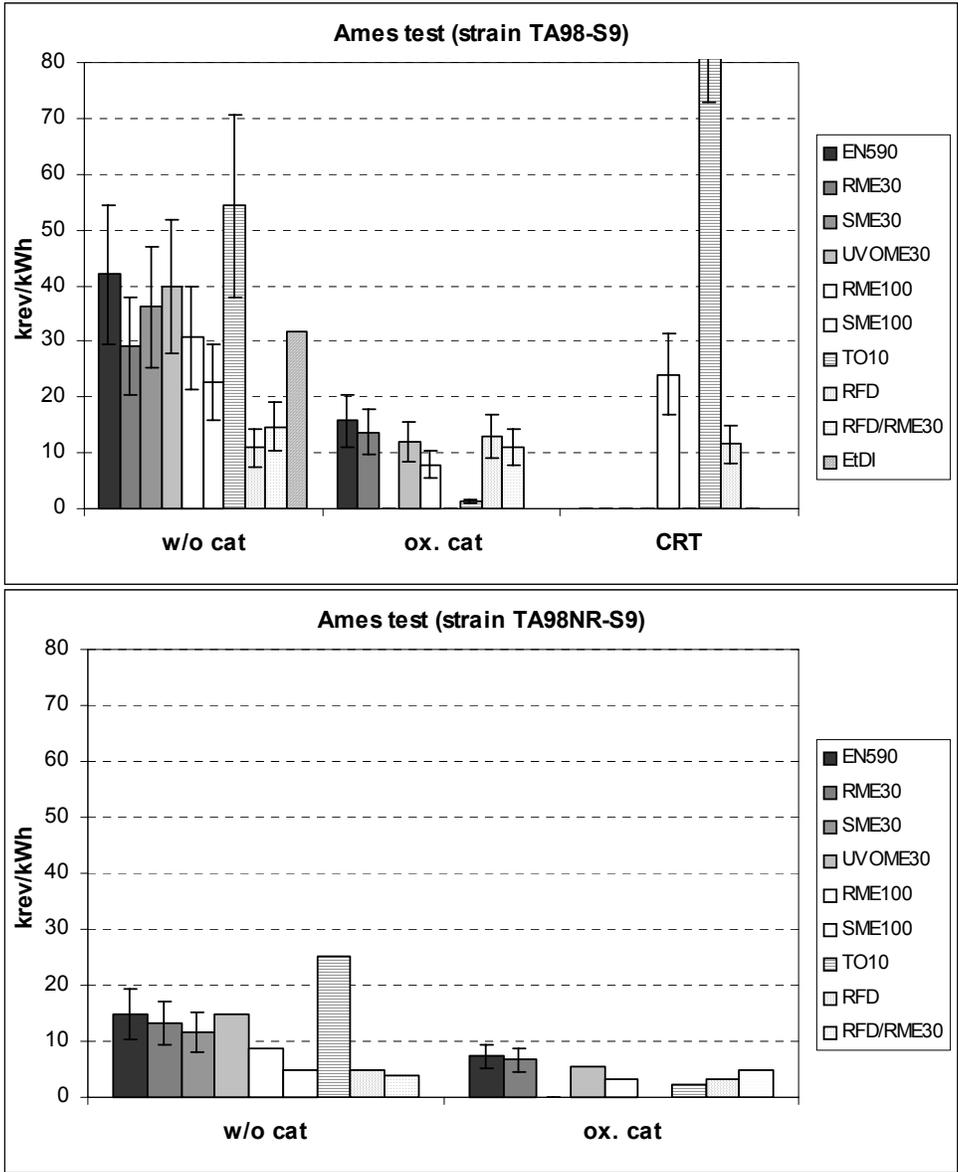


*Figure 32. Ames test results with Volvo engine, ECE R49 test.*

## 9.7 PARTICLE SIZE DISTRIBUTION MEASUREMENTS

### 9.7.1 General

Particle size distributions were measured from the exhaust gas of the Volvo bus engine using three different instruments, a BLPI impactor, a SMPS instrument and an electric ELPI impactor. The test fuels were EN590, RFD, EN590 fuel containing 30% RME (RME30) and RME100. The load mode 5 (intermediate speed, 75% load) of the ECE R49 test was used. The samples for the particulate size distribution measurements were taken from diluted exhaust gas as explained in chapter 6.2.4. The particle number distributions are shown per $cm^3$ diluted exhaust gas without correction of the dilution factor (around 11).

VTT has limited information on the total particulate mass results of mode 5 of ECE R49 test with the Volvo engine, as the standard practice is to collect particulate matter over the whole test. Hence, it was interesting to calculate the total mass results obtained with the BLPI impactor as g/kWh. The PM emission levels calculated from the BLPI measurements in mode 5 ranged 0.02 - 0.035 g/kWh, whereas the ECE R49 results varied from 0.03 to 0.08 g/kWh. In the engine mapping test (chapter **Error! Reference source not found.**) the particulate matter result at intermediate speed and 75% load was 0.032, which is very close to the level of the values obtained with the BLPI. EN590 gave the highest particulate emission result, whereas RME and RFD fuels gave the lowest results in the BLPI measurements.

### 9.7.2 BLPI results

The particle mass size distribution measurements using the BLPI impactor were repeated at least three times for each test fuel. In the most cases the total mass of the particles collected with the BLPI impactor varied from 0.3 to 0.6 mg. From test to test, variations in the results were observed. Most probably the variation was due to true differences in particle formation, even though the test conditions were kept constant in each run. The mass distributions that best represents the average of these runs were chosen from the 3 - 6 'identical' test runs.

The selected particle mass size distribution graphs are shown in Figure 33. It can be seen that the peak around the 100 nm is sharp for the RFD fuel in comparison with the other fuels. For the EN590 fuel, the peak was much broader. For the RME fuel the peak was low, but rather similar in shape as for the RFD fuel. However, particles larger than 0.5 μm (up to at least 10 μm) were also found for the RME fuel. Typically the impactor filters were brighter for the RME fuel compared to the other fuels. This is indicative of a smaller black carbon mass fraction from the RME fuel than from hydrocarbon fuels. The EN590 fuel containing 30% RME resulted in a mass distribution curve, that was more or less in between the distribution curves for the EN590 and RME fuels. However, the first peak for the EN590/RME30 fuel seemed to follow a pattern similar to that for the EN590 fuel, whereas the second "peak" (2 - 4 μm) might indicate large

particles with the RME fuel.

The total particulate mass concentrations of the RME fuel were significantly lower than those of the EN590 fuel. However, a comparison of the results with virtual impactor and the BLPI-impactor indicates that some organic matter is evaporated from BLPI. Formation of black carbon and quantification of evaporative losses of particulate matter are items requiring further research in future experiments with the biodiesel fuels.
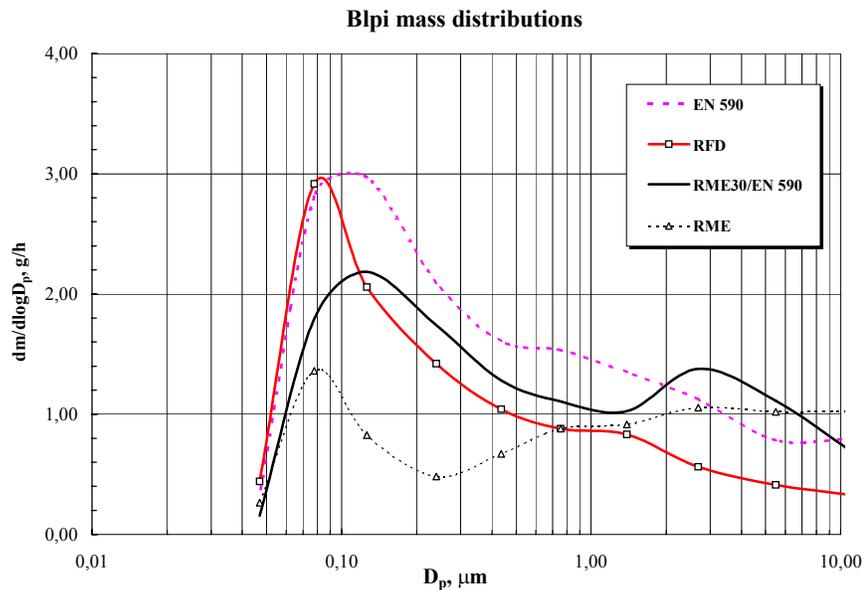
**Blpi mass distributions**



*Figure 33. Selected Blpi mass distributions (aerodynamic diameter) with test fuels, Volvo. Intermediate speed, 75% load (mode 5 of ECE R49 test).*

### 9.7.3 SMPS and ELPI number size distributions

Simultaneously with the BLPI measurements  SMPS and ELPI instruments were used to measure the number size distributions. The sampling point was the same as used in the BLPI measurements, and no additional dilution was used. The ELPI is a real-time instrument and it was operated continuously. Multiple scans were made with the SMPS instrument for each of the fuels. The repeatability of the test runs was good.

The number size distributions measured for the different fuels are shown in Figure 34. ELPI and SMPS instruments are based on different sizing principles, and no direct comparison can be made without adjusting the results of particle densities. However both results indicate similar trends. The RFD fuel has no ultrafine nucleation mode below 40 nm. For other fuels the nucleation mode is clearly present. This mode adds very little to the particulate mass generated, and hence was not seen in the BLPI measurements.

The absence of the nucleation mode is probably due to the very low sulfur content of the RFD fuel. In literature it has been stated that nucleation mode products are condensates of sulfuric acid, water and hydrocarbons [32, 33], which is in accordance with the results obtained in the measurements of this study. The nucleation mode may disappear, if the diluted exhaust gas is reheated or dried - also the dilution ratio has an effect on the nucleation mode [32, 33]. The effect of dilution ratio on the nucleation mode was also observed in some additional measurements carried out during the test period. Research on this phenomenon was beyond the scope of this work, and therefore the test conditions were kept constant in all measurements presented in this report.

The concentration of particles around 0.1 µm was lower for the RME based fuels supporting the BLPI results, in which lower mass concentrations were measured for the RME fuels. The size distribution curve of RME30 also falls between the curves of RME100 and EN590 as was the case with the BLPI results. For the RFD fuel, the ELPI measurements indicate higher concentration of particles around 0.1 µm than for the EN590 fuel, contrary to the SMPS measurements. Differences between the ELPI and SMPS size distribution results are most likely due to different principles of particle sizing method. E.g. differences in effective particle density in particles originating from different fuels will affect the results [34].
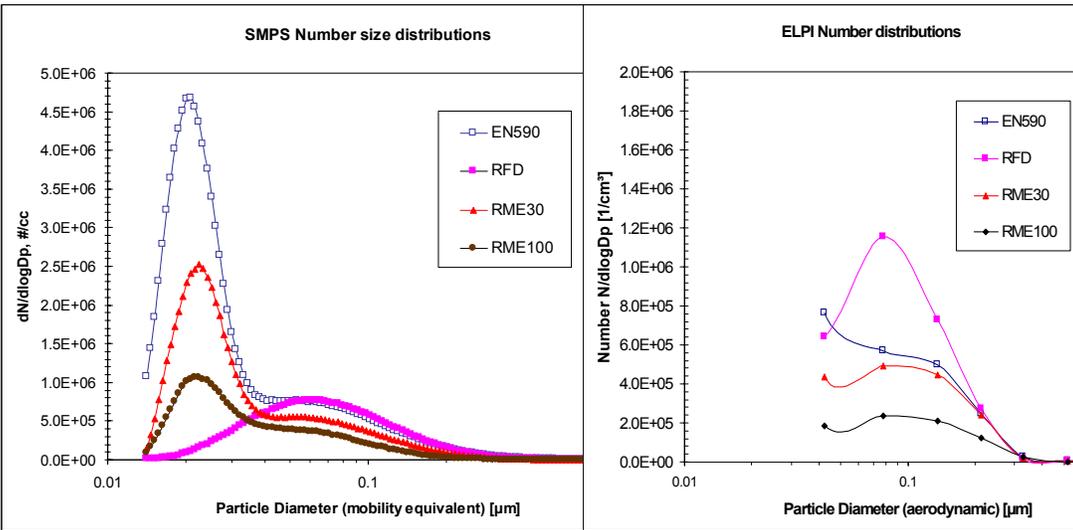


*Figure 34. ELPI and SMPS number size distributions for different fuels.*

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## 9.8 SUMMARY OF THE EFFECT OF ESTERS ON THE EMISSIONS WITH VOLVO

The effect of esters (RME, UVOME, SME) on the regulated emissions, on the sum of 14 PAHs in particulate SOF and semivolatile phase and on the mutagenicity of particulate SOF is summarized in Figures 35 and 36. RME30, SME30, UVOME30, RME100 and SME100 were compared with EN590. RFD/RME30, RME100 and SME100 were compared with RFD.

Bioesters reduced the CO and HC emissions compared to the hydrocarbon fuels in the tests without the aftertreatment devices. The absolute differences in the CO and HC emissions were low, and hardly any signigicant effect was seen, when the aftertreatment devices were used.

Adding 30% ester in the EN590 fuel did not affect the $NO_x$ emission significantly, whereas neat esters resulted in a clear increase. The $NO_x$ emission increased linearly when RME was compared with the RFD fuel. The difference in $NO_x$ emission between RFD and the neat RME was greater than the difference between EN590 and the neat RME. The effect of bioesters on the $NO_x$ emission was similar both with and without aftertreatment devices.

Clear reductions in PM emissions with esters were noted in tests without aftertreatment devices and with the oxidation catalyst. The PM emissions with CRT were at the same (very low) level with RFD, RFD/RME30 and RME100. The absolute differences in PM emissions with the EN590 fuel and the neat esters were the greatest in the tests with the oxidation catalyst, in which the low sulfur content of esters gave additional benefit.

A reduction in level of 14 PAHs in the particulate SOF was observed in the tests without catalyst when esters were compared with the EN590 or the RFD fuels. Similar effect was seen for the PAHs in the semivolatile phase, when esters were compared with the EN590 fuel, but no benefit of ester was seen when compared with the RFD fuel. The esters did not affect significantly the PAH emissions when aftertreatment devices were used.

The esters gave lower mutagenicity of particulate SOF when compared to the EN590 fuel. When esters were compared to RFD fuel, benefit was seen only in the tests with the oxidation catalyst. Neat esters gave higher Ames results than RFD in the tests without catalyst and with the CRT catalyst/trap.

There was no significant differences in exhaust emissions when RME, SME and UVOME were compared with each other.
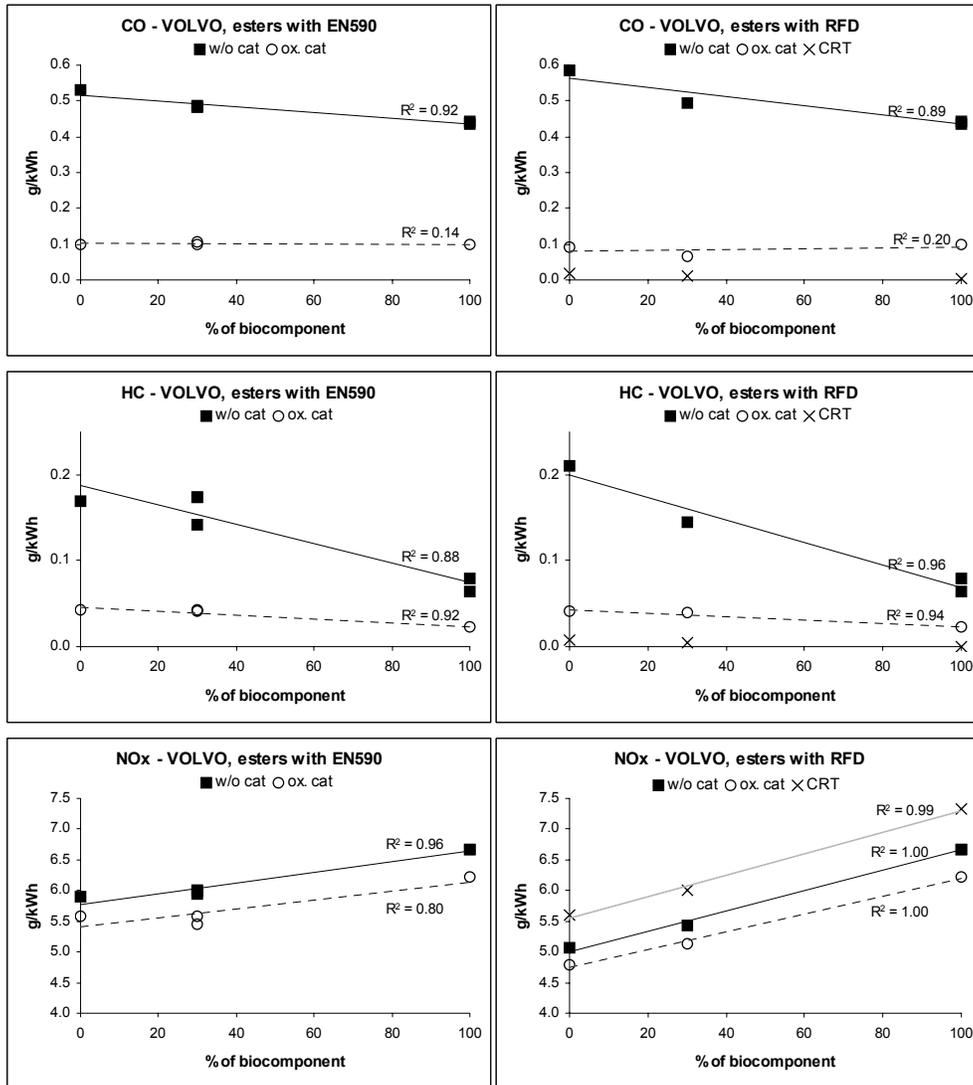
*Figure 35. The effect of esters on regulated gaseous emissions with Volvo, ECE R49 test.*
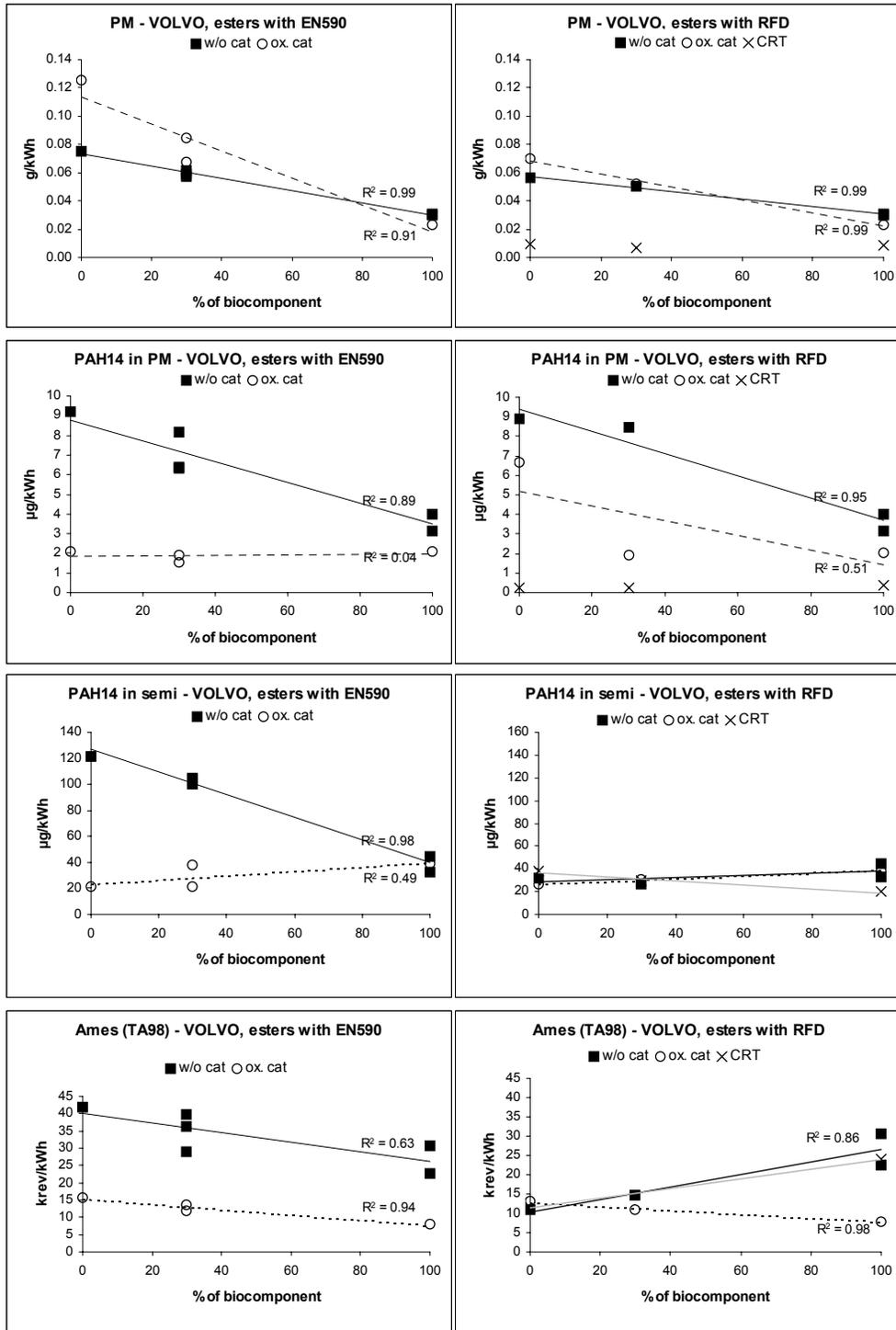
*Figure 36. The effect of esters on PM and PAH emissions and on Ames mutagenicity of particulate SOF with Volvo, ECE R49 test.*

# 10    RESULTS WITH MD VALMET ENGINE

The numerical results of the emission tests with the Valmet engine are presented in Appendix 10. The results over ECE R49 test are shown in Figures 37 - 38.

The HC emission level with the Valmet engine was about 2.5 times higher, the CO emission level 4 times higher and the PM emission 5 times higher than the respective emissions of the Volvo engine. The $NO_x$ emission was only slightly higher with the Valmet engine compared to the Volvo engine.

Adding 30% RME to the EN590 fuel or swiching to the TO10 fuel resulted in benefits regarding the CO and PM emissions, but adverse effects on the $NO_x$ emission. 30% RME in the EN590 fuel increased the $NO_x$ emission by about 5%, but decreased the PM emission by more than 20%.

The EtDI fuel resulted in a significant reduction (45%) of PM emission when compared to the EN590 fuel. The $NO_x$ emission level was also lower (4%) with EtDI fuel than with the EN590 fuel. The HC emission was 30% higher, but the CO emission 10% lower with the EtDI fuel than with the EN590 fuel, which is a trend different from that with the Volvo engine. With the Volvo engine the CO and HC emission levels were 2.5 - 3 times higher for the EtDI fuel than for the EN590 fuel.

When reformulated diesel fuel was used in the Valmet engine, the CO emission was higher, but the $NO_x$ and PM emissions were lower than using the EN590 fuel. The benefit in PM emission was 25% with RFD compared to the EN590 fuel.

The formaldehyde emission level was generally higher with the Valmet engine than with the Volvo engine (Figure 39), except for the EtDI fuel, which resulted in the same formaldehyde emission level in both engines. The formaldehyde emission with the EtDI fuel was higher than with the other fuels for both engines. Bioesters or the TO10 fuel did not affect the formaldehyde emission with the Valmet engine.

Similarly to Volvo, the concentration of nitrous oxide, ammonium and individual hydrocarbons (except n-octane) did not exceed the detection limit of the FTIR equipment.
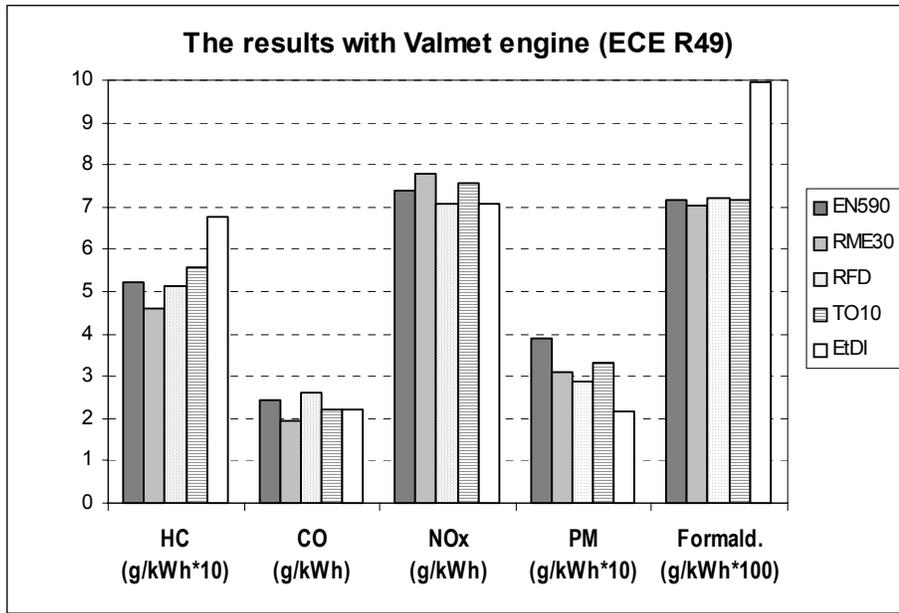
*Figure 37. HC, CO, NO$_x$, PM and formaldehyde emissions with Valmet engine, ECE R49 test.*
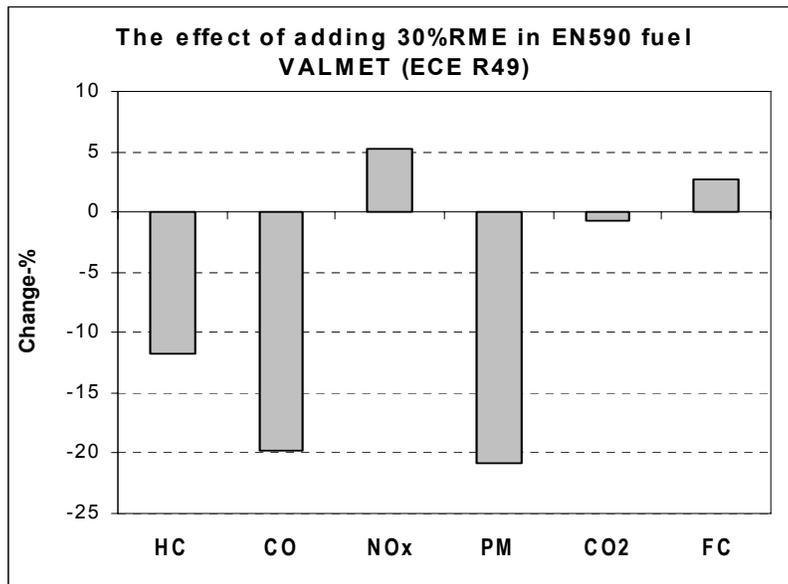


*Figure 38. Changes in regulated emissions, CO$_2$ and fuel consumption when 30% RME is added to EN590 fuel, Valmet engine, ECE R49 test.*
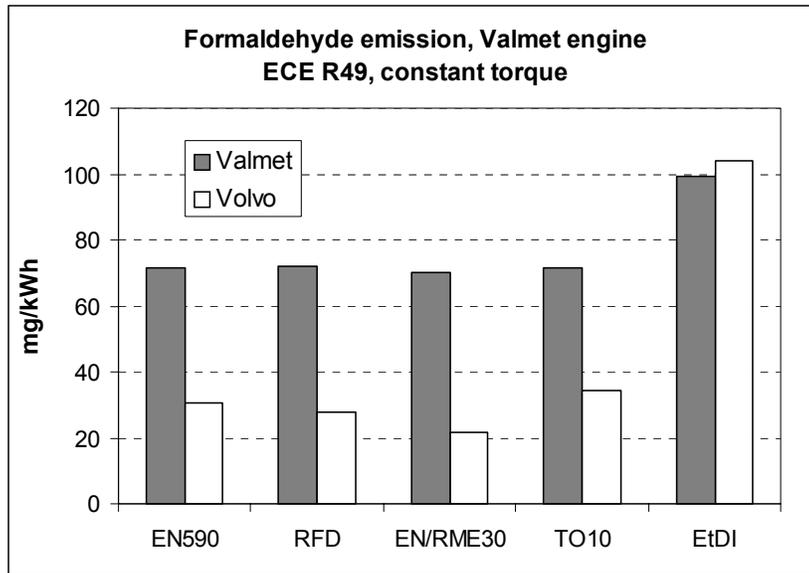
*Figure 39. Formaldehyde emissions with Valmet and Volvo engines, ECE R49 test.*

# 11    TESTS WITH AUDI VEHICLE

## 11.1    TEST CYCLES

The major part of the tests with the Audi vehicle was carried out according to the US FTP75 test cycle with the catalyst of the vehicle in place. A couple of tests were run with the European test cycle, and some tests according to the FTP75 cycle were also run without catalyst. The tests were carried out at +23 °C.

The test cycles were divided into three sub-cycles for sampling (Figure 40). The first part of the FTP cycle is 0 - 505 seconds, the second part 505 - 1372 seconds and the third part (after a 10 minutes stop) again  last 505 seconds. The first part of the European test included the first two individual sub-cycles of the urban cycle (ECE15), the second phase was the rest of the ECE15 cycle, and the third part was the extra urban portion (marked as EUDC).

About 2/3 of the European test cycle is composed of very low speeds and smooth accelerations, whereas the FTP cycle is more "rough". As a consequence, an oxidation catalyst operates properly longer time periods during the FTP test cycle than during the European test cycle.
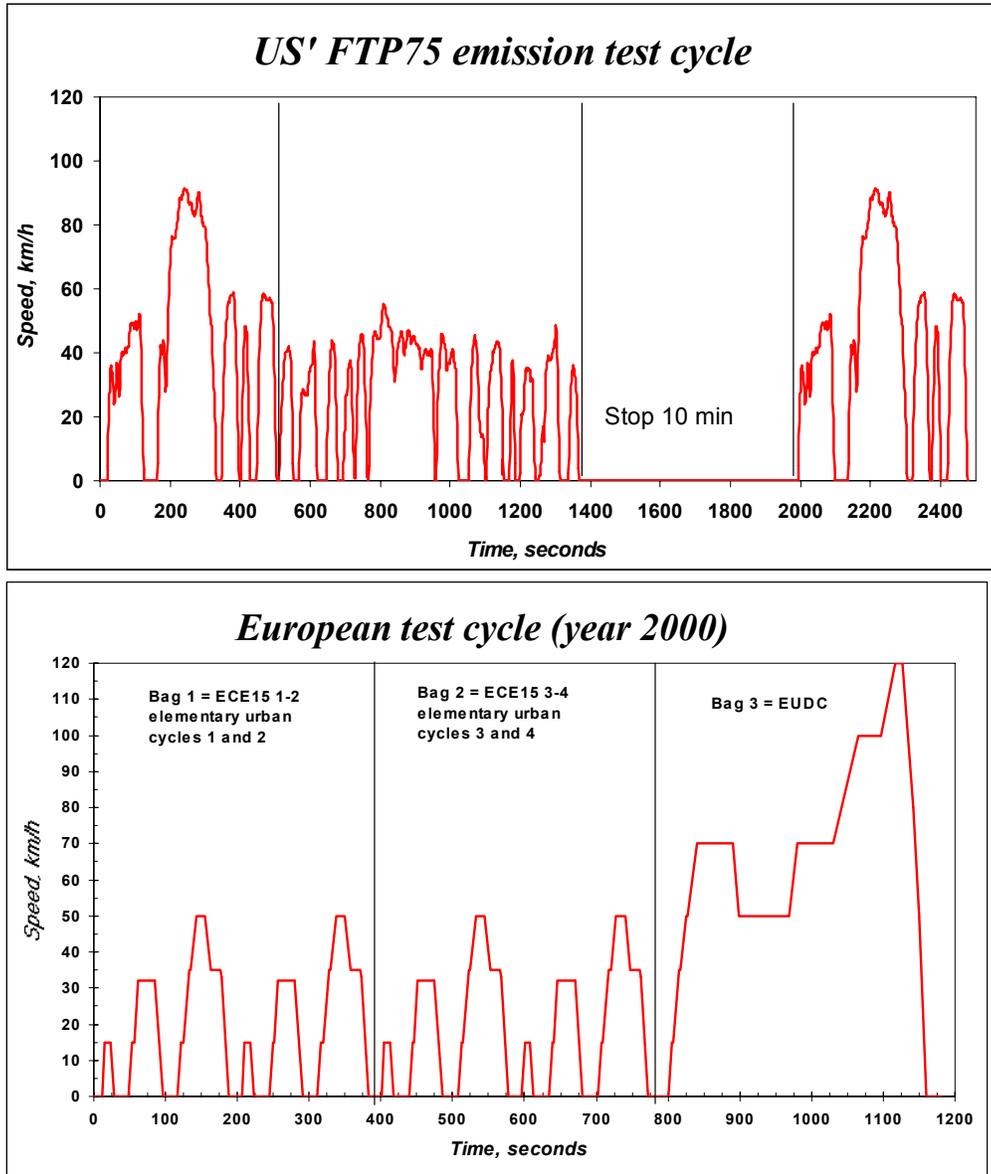
*Figure 40. US FTP75 and European test cycles used in the light-duty emission tests with Audi vehicle.*

## 11.2 COMPARISON OF EUROPEAN AND FTP75 TEST CYCLES

The numerical results with the European and US FTP75 test cycles for the EN590 and RME30 fuels are shown in Table 9.

*Table 8. The emission results with European and US FTP75 test cycles for EN590 and RME30 fuels, Audi with the catalyst.*

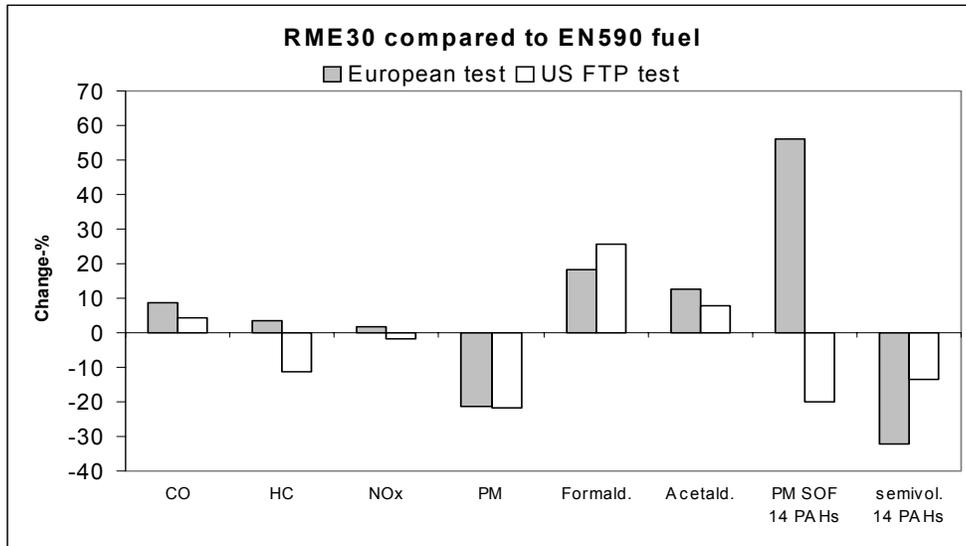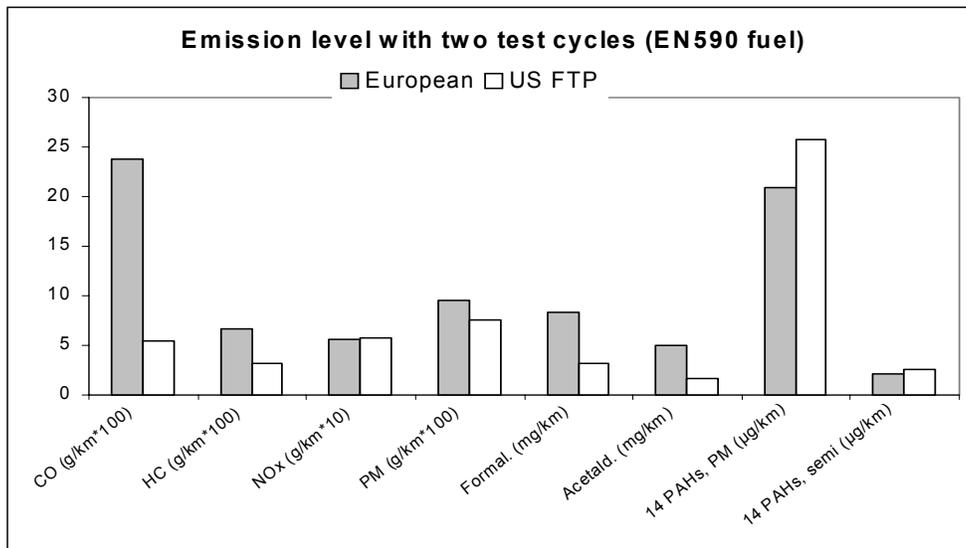| | CO | HC | NOx | PM | Formald. | Acetald. | 14 PAHs PM SOF | 14 PAHs semivol. |
|---|---|---|---|---|---|---|---|---|
| | g/km | g/km | g/km | g/km | mg/km | mg/km | µg/km | µg/km |
| European test cycle | | | | | | | | |
| EN590 | 0.24 | 0.066 | 0.57 | 0.096 | 8.3 | 5.0 | 21 | 2.1 |
| RME30 | 0.26 | 0.069 | 0.58 | 0.075 | 9.8 | 5.6 | 33 | 1.4 |
| US FTP75 test cycle | | | | | | | | |
| EN590 | 0.055 | 0.032 | 0.58 | 0.088 | 3.2 | 1.7 | 26 | 2.5 |
| RME30 | 0.058 | 0.028 | 0.57 | 0.069 | 4.0 | 1.8 | 21 | 2.2 |



*Figure 41. Results with European and US FTP75 test cycles with Audi (catalyst equipped) and differences when RME30 fuel is compared to EN590 fuel.*

CO, HC, particulate matter and aldehyde emissions were higher with the European than with the FTP75 test cycle (Figure 41). The reason for that was most probably the low speeds in the European test cycle, which means that the oxidation catalyst works properly over a shorter time period in the European test than in the FTP75 test. $NO_x$ emissions were at the same level with both cycles, but PAH emissions seemed to be lower with the European than with the US FTP75 test cycle.

Regarding CO, $NO_x$, PM, aldehyde, and semivolatile PAH emissions the differences between the EN590 and the RME30 fuel seem to be similar with the European and FTP75 test cycles. The results obtained for HC and PAHs in particulate SOF with the European test cycle were not in line with the US FTP75 test cycle. However, it should be noted that the PAH emissions in the tests with the catalyst were too low to draw any conclusions.

## 11.3    TEST RESULTS

### 11.3.1  Regulated emissions

The numerical results of the emission tests with the Audi vehicle are presented in Appendix 11.

The absolute $NO_x$ emission level was about the same both with and without catalyst (Figure 42). Particulate emissions were slightly higher in the tests without oxidation catalyst than with it.

In most diesel-fuelled engines and vehicles vegetable oil esters cause an increase in $NO_x$ emissions compared to hydrocarbon fuels. With the Audi TDI vehicle the situation seems to be different. When mixtures of vegetable oil esters were compared to respective hydrocarbon fuels, it was observed that no significant difference in $NO_x$ was found (Figure 43). In some cases the $NO_x$ emission even decreased with esters. Especially, when 30% RME was blended with the RFD fuel, the decrease in $NO_x$ emissions seemed to be significant.

The fuel containing ethanol (EtDI) resulted in an increase in $NO_x$. The EtDI fuel was not available when the actual test programme was carried out, and some changes in the emission level of the vehicle itself are possible. Therefore no relative difference numbers are shown in the figures. However, the absolute difference in the $NO_x$ emission was so high that it is evident that the $NO_x$ emission increased with the Audi 1.9 TDI vehicle when the EtDI fuel was compared to the other fuels. In a Finnish study it was previously observed that density and viscosity seem to have a different effect on the $NO_x$ emission of the Audi TDI engine than on other diesel engines [35]. The previous IEA/AMF Annex X also showed the similar trend [14].

The fuel affected the particulate matter emission of the Audi 1.9 TDI vehicle considerably. The particulate matter emission was 15 - 25% lower for the fuels

containing vegetable oil esters than for the respective hydrocarbon fuels. The EN590 fuel produced the highest particulate emissions. The most significant reduction in particulate emission was observed for the EtDI fuel.
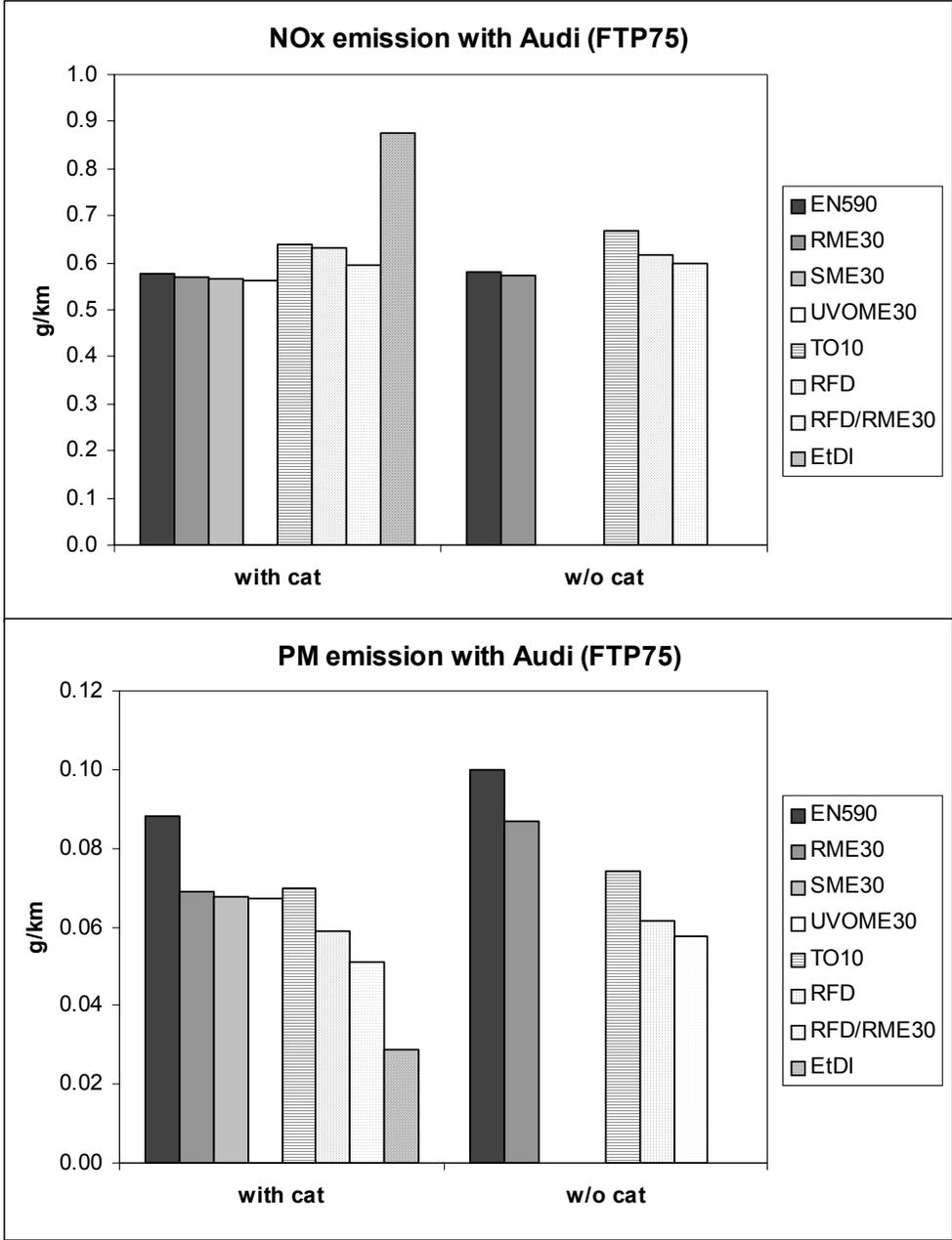


*Figure 42. NO$_x$ and PM esmission results with Audi vehicle (FTP75 test).*
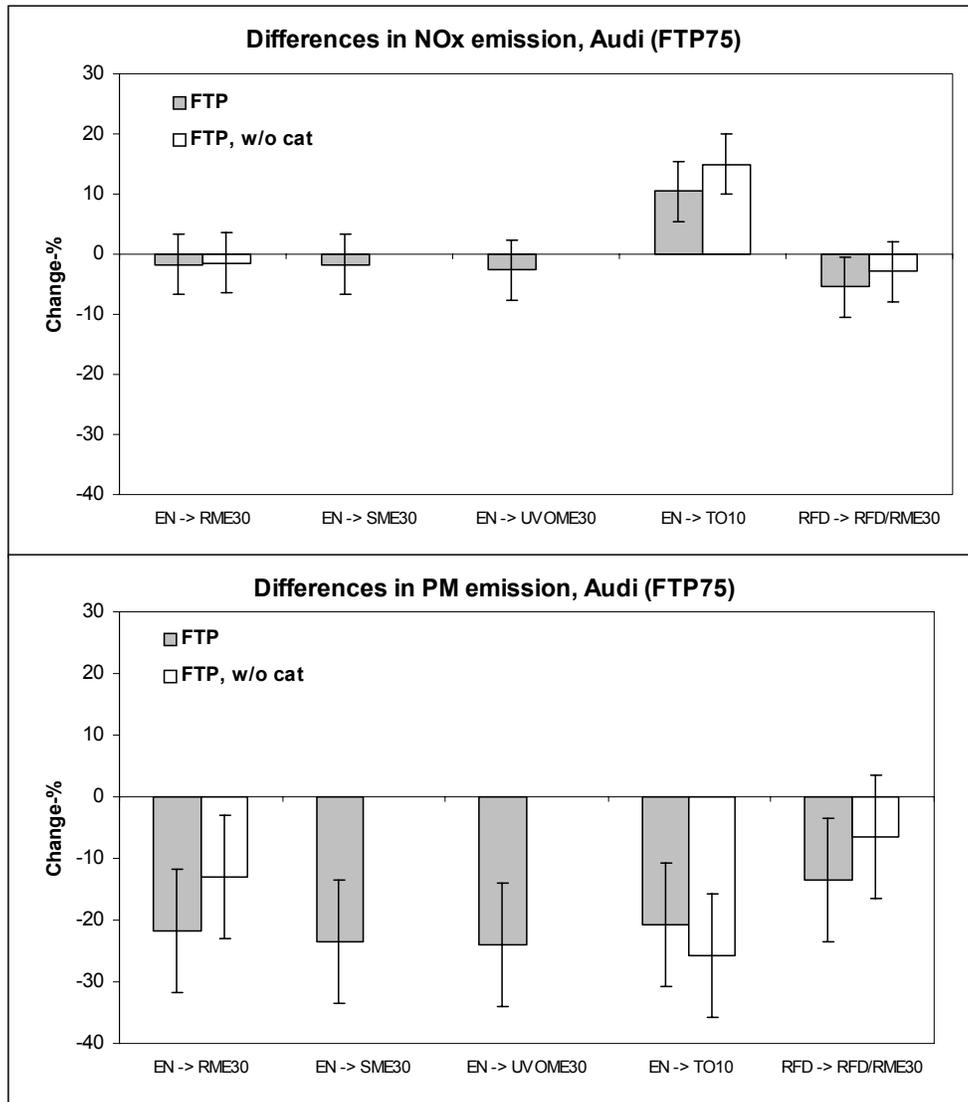
*Figure 43. The differences in $NO_x$ emission between test fuels, Audi vehicle. General deviation for $NO_x$ (5%) and PM (10%) are shown as error bars.*

The oxidation catalyst effectively reduced CO and HC emissions (Figure 44). The reduction in the CO emission was around 90% and for HC emission around 70%.

The CO and HC emission levels of the Audi 1.9 TDI vehicle were very low, and consequently, the absolute differences in CO and HC emissions were low, as well. The only differences that might be significant, were the low CO emission with the UVOME fuel and a lower HC emission level with esters than with hydrocarbon fuels. In addition, HC level with the UVOME fuel seemed to be lower than with RME or SME fuels. The EtDI fuel resulted in higher CO and HC emission levels than the EN590 fuel.

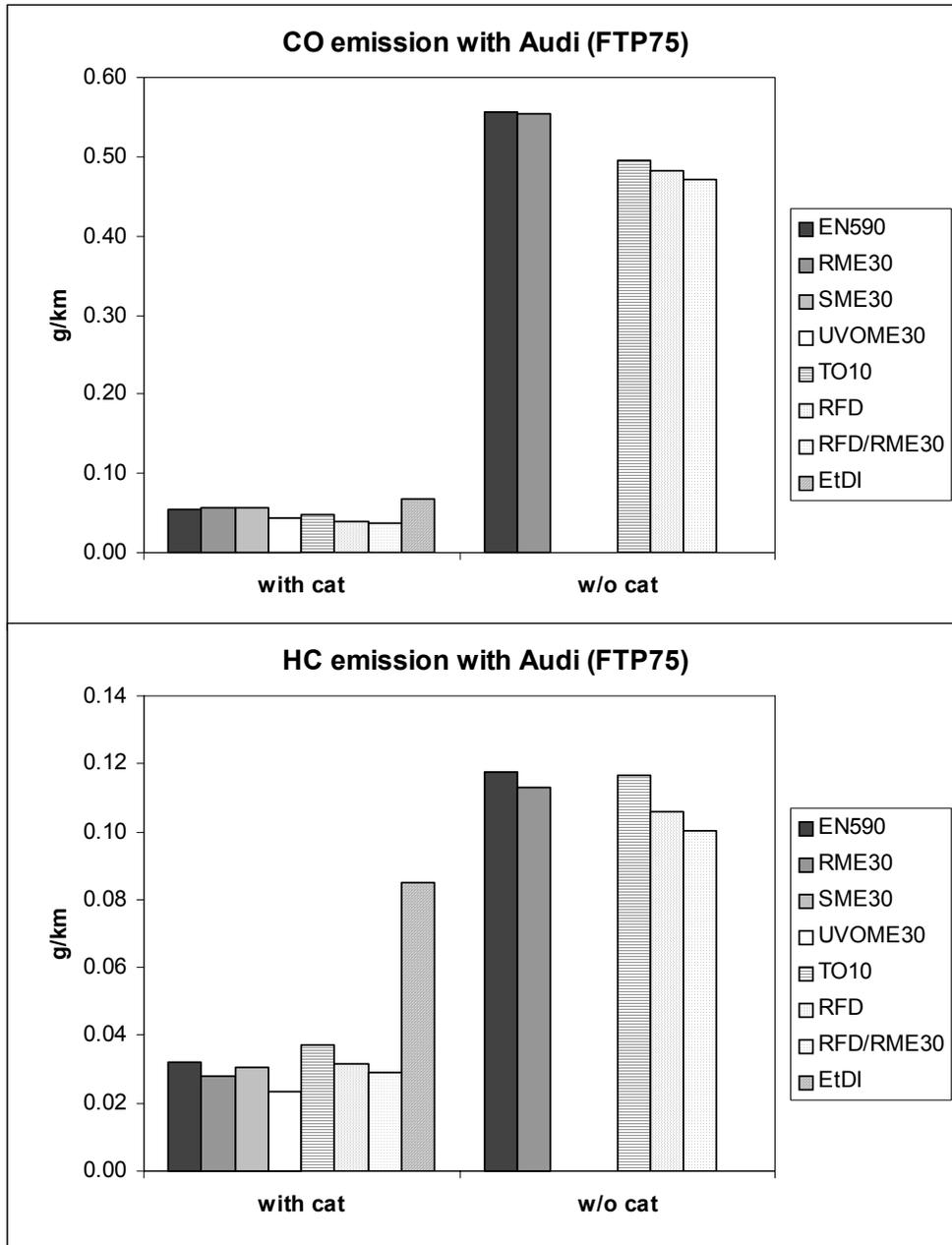*Figure 44. CO and HC emissions with Audi vehicle.*

## 11.3.2 Aldehydes and speciated hydrocarbons

Numerical results of aldehyde measurements are shown in Appendix 11. The formaldehyde and acetaldehyde emissions represented 70 - 90% of the total aldehyde emissions. The emission level of aldehydes other than formaldehyde and acetaldehyde was too low to reliably compare different fuel qualities with each other.

The oxidation catalyst reduced aldehyde emissions significantly. The reduction of formaldehyde was 60 - 70% and reduction of acetaldehyde 50 - 60%.

Bioesters resulted in a clear increase in formaldehyde emission (Figure 45). The increase seemed to be less significant for UVOME than for RME and SME, or for a blend with the reformulated fuel. The change was relatively small when blending RME into RFD. The fuel with tall oil component did not change formaldehyde emissions when compared to EN590.

The comparison of the acetaldehyde emission with different fuels was not as evident as formaldehyde emission. The absolute emission level of acetaldehyde was about 30 - 60% of the emission level of formaldehyde. The low absolute emission levels increase the relative uncertainty in the results. It seemed that the only changes that may exceed the uncertainty limit would be the lower acetaldehyde emission with TO10 than with the EN590 fuel.

The emission levels of aldehydes other than form- and acetaldehyde were almost below the detection limit. However, it should be noted that generally the benzaldehyde emission was at maximum with the EN590 fuel, which also contained the highest level of aromatics.

The hydrocarbon emissions are in general very low with diesel-fuelled light-duty vehicles, and this also applies for individual hydrocarbon components. This was also the case with the Audi vehicle. The methane emission and the sum of benzene, ethylbenzene, toluene and xylenes (BTX) were below 10 mg/km (Figure 46), whereas these values can easily be tenfold with gasoline-fuelled vehicles. 1.3-butadiene was below the detection limit in the exhaust emissions of the Audi vehicle.

It was interesting to observe that the BTX emission seemed to be higher with the EN590 fuel than with the other fuels, which is probably directly connected to the higher aromatics content of the EN590 than of the other fuels.
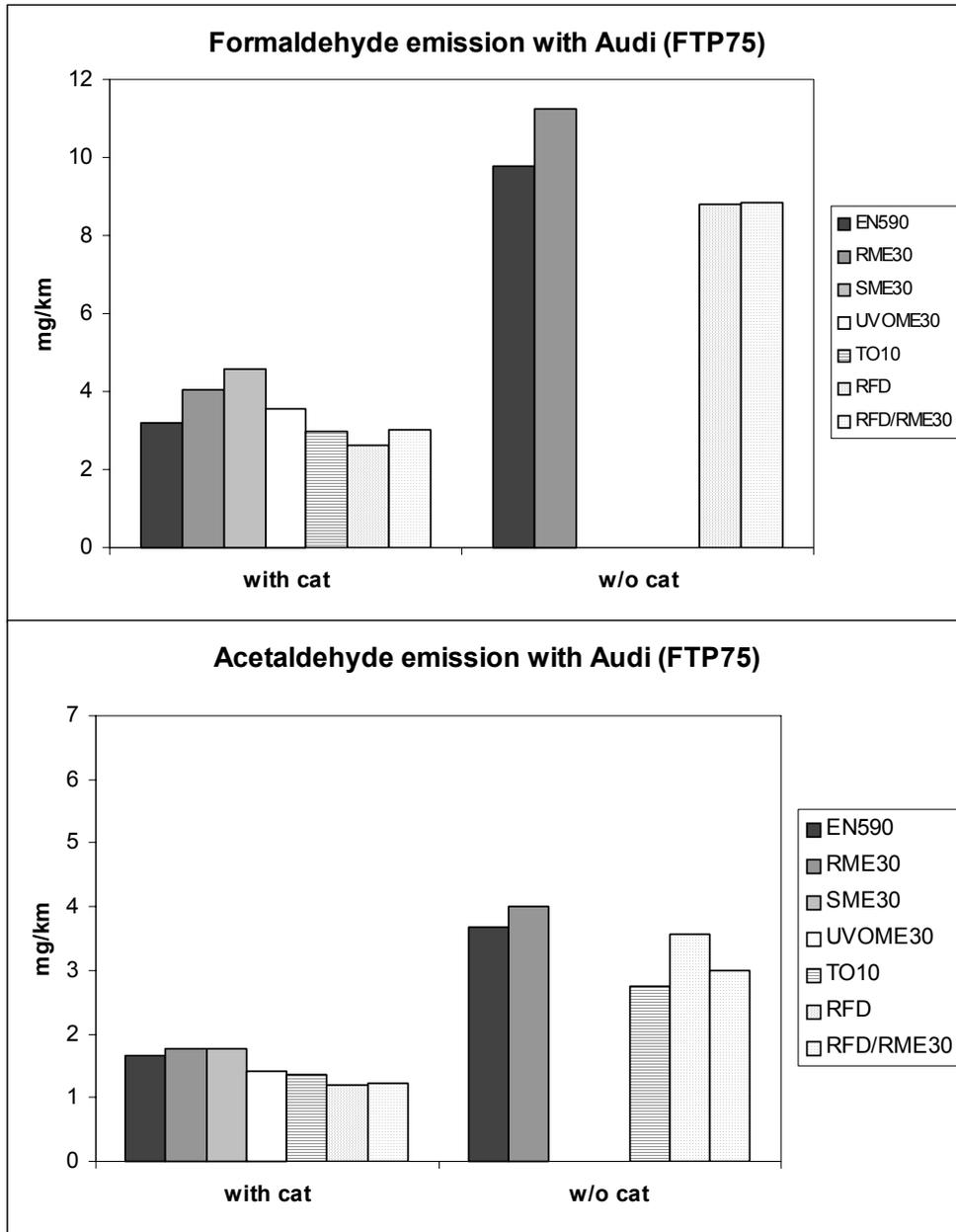
70

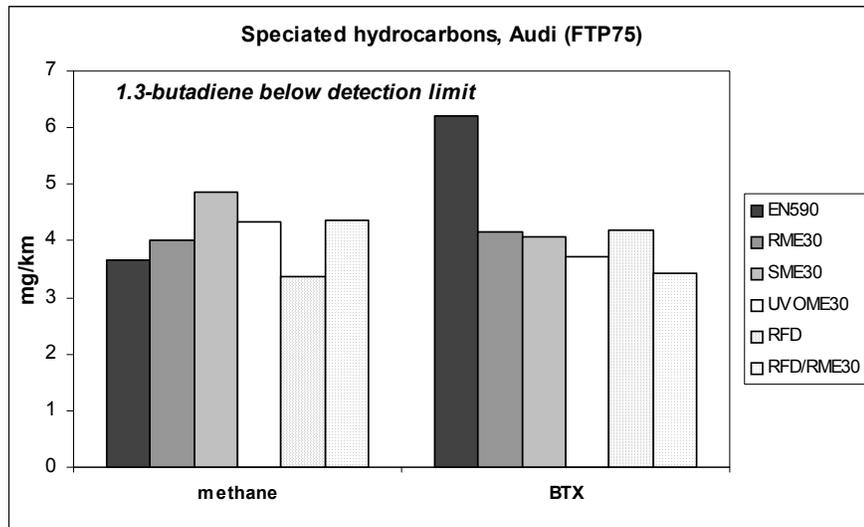*Figure 45. Formaldehyde and acetaldehyde results with Audi vehicle.*

*Figure 46. Methane and BTX emissions with Audi vehicle.*

## 11.3.3  Composition of particulates

The particulates from the Audi vehicle were rather "dry". The soluble organic fraction (SOF) was generally only 10±5% of the total particulates. The deviation in the SOF analysis was too high to draw conclusions from the effect of catalyst or fuel on SOF results. Hence, it was not possible to study "black carbon" portion either.

The particulates contained about 1% of sulfates and combined water with all fuels with and without the oxidation catalyst.

## 11.3.4  PAH compounds in particulate and semivolatile phase

The numerical results of the PAH analysis are given in Appendix 12.

The oxidation catalyst reduced the amount of PAH compounds in particulates when the average values for all fuels are considered. However, many discrepancies were observed. Eg., it can be seen from Figure 47 that no significant difference is found in the sum of 14 PAH compounds in the tests without or with catalyst for EN590 and RFD/RME30 fuels. On the other hand, the effect of catalyst was clear for the RME30, TO10 and RFD fuels. It is evident, however, that the catalyst effect in most cases overruns possible fuel effects.

The effect of fuel on 14 PAHs in the particulate phase was not consistent. It seemed that the esters gave a lower PAH level than the EN590 fuel in the FTP test with catalyst. However, no benefit of RME was seen when it was blended in the RFD fuel.

The level of selected 14 PAHs in the semivolatile phase was so low that no effect

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of catalyst, test cycle or test fuels was seen.



**Sum of 14 PAHs in PM SOF, Audi (FTP75)**

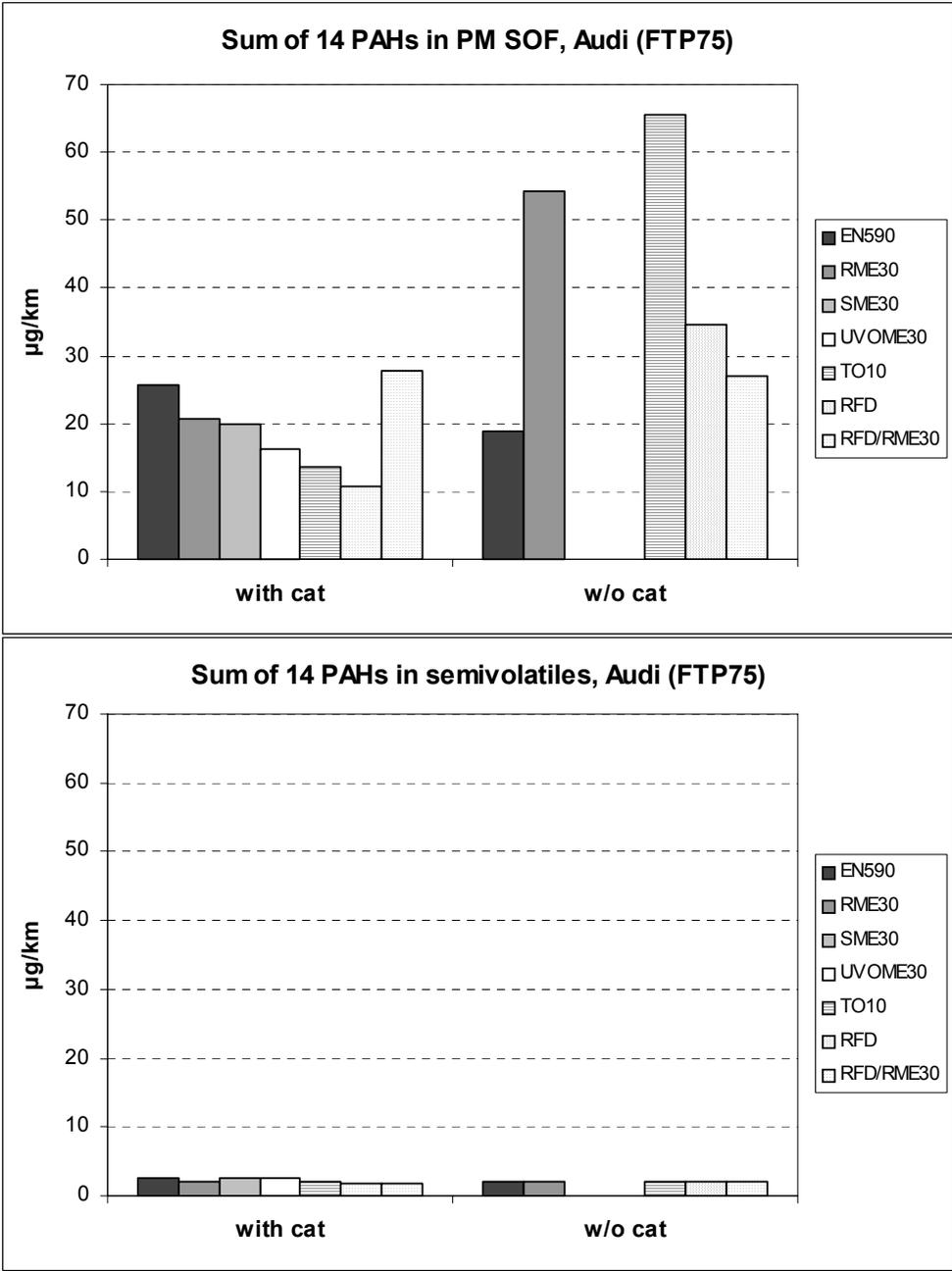**Sum of 14 PAHs in semivolatiles, Audi (FTP75)**

*Figure 47. Sum of 14 PAH compounds analysed from particulate SOF and semivolatile phase, Audi (FTP75 test).*

## 11.3.5 FTIR results

On-line FTIR measurements were carried out with the Audi vehicle during selected FTP tests.

The compounds that exceeded the detection limit were: $NO_2$ (only in the tests without catalyst), formaldehyde, methane, ethene and n-octane. Nitrous oxide ($N_2O$) exceeded the detection limit occasionally. Ammonium and most individual hydrocarbons (e.g. benzene, 1.3-butadiene, propene) were well below the detection limit.

Formation of nitrogen dioxide, nitrous oxide, formaldehyde and n-octane is shown in Figures 48 and 49. For these compounds, the general deviation was some 10% in the tests with the same fuel.

$NO_2$ was observed only in the tests without catalyst. RFD, RFD/RME30 and TO10 gave a slightly higher $NO_2$ level than the other fuels.

The nitrous oxide level was slightly higher in the tests with the catalyst than without it. However, $N_2O$ concentrations were mainly below the detection limit.

Formaldehyde and n-octane levels were higher in the tests without catalyst than with catalyst. The order of the fuels was generally similar to those reported in chapters 11.3.1 and 11.3.2 for total hydrocarbons and formaldehyde. RME seemed to result in a slightly higher formaldehyde emissions than the base fuels. A large amount of formaldehyde was formed during the first three minutes. After that formation was not as strong, except at the end of the test.
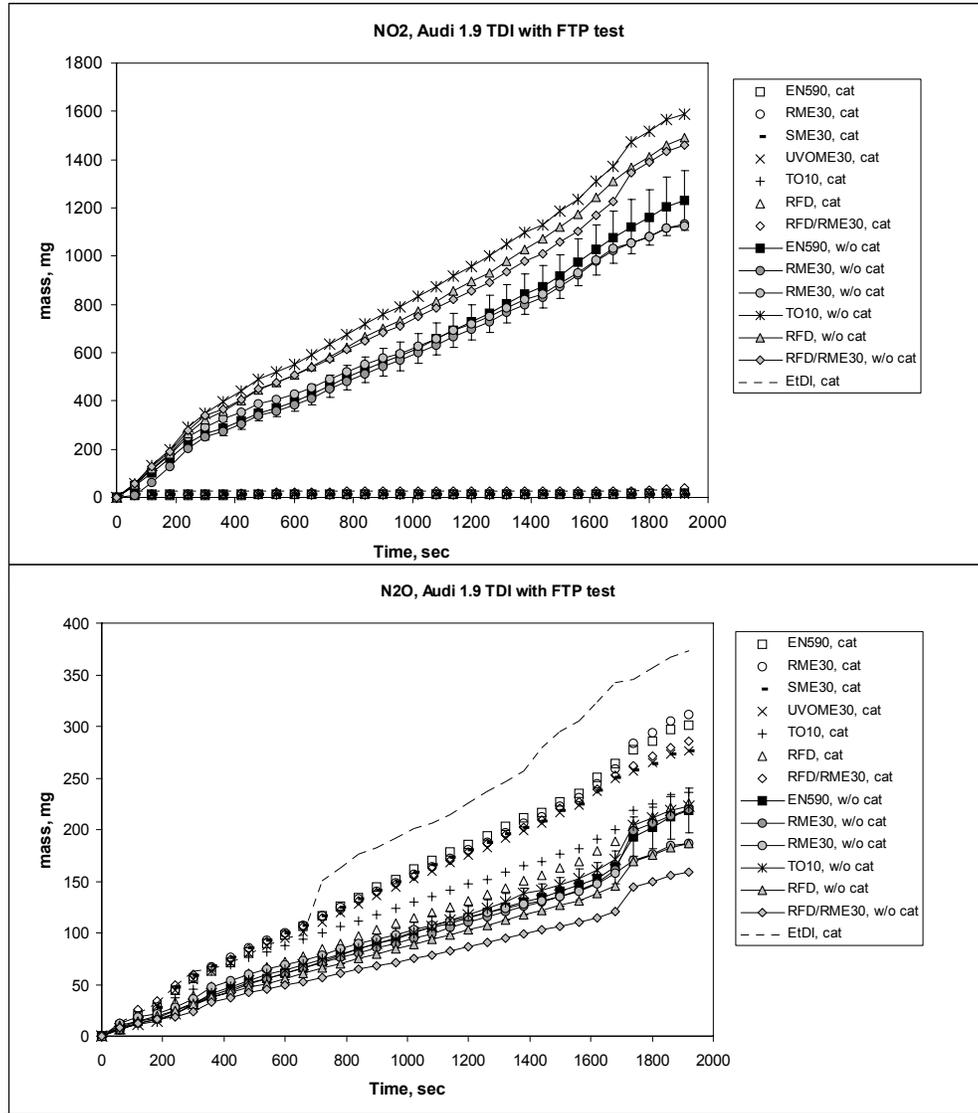
*Figure 48. Cumulative mass of NO$_2$ and N$_2$O during FTP test with Audi vehicle.*
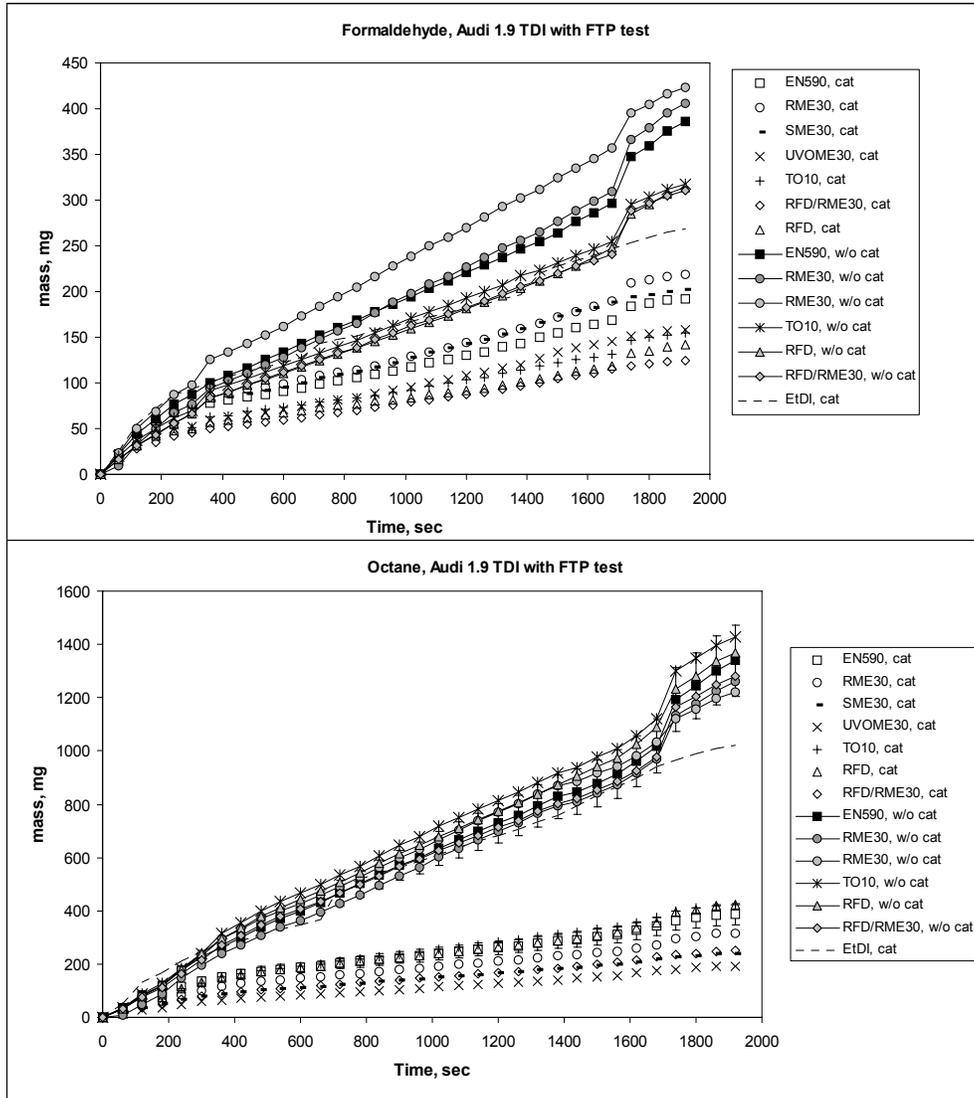
*Figure 49. Cumulative mass of formaldehyde and n-octane during FTP test with Audi vehicle.*

# 12    SUMMARY

The IEA/AMF Annex XIII "Performance of biodiesel" was carried out in 1998 and 1999. The participants of the project were Belgium, Canada, Finland, Japan, Sweden, USA, and the Netherlands. The work of Annex XIII was carried out both at ORNL and at VTT. This report includes only VTT's results. A summary report on the results of both laboratories will be prepared later.

The target of the project was to perform an extensive analysis of exhaust gas with biodiesel and new engines. The major part of the tests was carried out with a Euro 2 emission level Volvo bus engine. Tests were made without a catalyst, with an

oxidation catalyst and with a CRT catalyst/trap. Some tests were also carried out with a medium-duty Valmet tractor engine and with a light-duty Audi TDI vehicle. Several test cycles were used. In addition, engine mapping tests were carried out with the Volvo and the Valmet engine.

The vegetable oil esters studied were rapeseed methyl ester (RME), soy bean oil methyl ester (SME) and used vegetable oil methyl ester (UVOME). RME and SME were tested as 30% blends in European grade diesel fuel (EN590) and as neat esters. RME was also blended (30%) into Swedish Environmental Class 1 diesel fuel (RFD). The fuel matrix also included a Canadian diesel fuel blended with 10% hydrated tall oil (TO10) and an emulsion of Swedish Environmental Class 1 diesel fuel and some 15% ethanol (EtDI).

The summary of the effect of bioesters on regulated and unregulated emissions is shown in Table 10. Compared to hydrocarbon fuels bioesters reduced CO and HC emissions in most cases. However, the absolute differences were low when aftertreatment devices were used with the bus engine (close to zero emission level). The EtDI fuel resulted in a significant increase in CO and HC emissions with the bus engine and the TDI vehicle.

Adding 30% ester in the EN590 fuel did not affect the $NO_x$ emission significantly, whereas neat ester resulted in an increase of around 10%. When 30% ester was blended into the RDF fuel, the $NO_x$ emission increased by 5…7% with the bus and the tractor engine, but decreased by about 5% with the TDI vehicle. The EtDI fuel resulted in a lower $NO_x$ emission than the EN590 fuel with the bus engine, but higher emission with the TDI vehicle.

Clear reductions in PM emissions were noted with almost all technologies, when esters were blended into the EN590 or RFD fuel. The engine mapping tests showed that a RME blend generally results in a lower PM emission than the base fuel with the exception of idle conditions. The RME blend resulted in higher PM emissions with the Japanese test cycle, which includes a lot of idle running. Black smoke was low with bioester fuels. The EtDI fuel reduced PM emissions compared with the EN590 fuel. The PM emission with the CRT catalyst/trap was too low to draw conclusions of the effect of fuel.

The particulate matter consists of, i.a., "black carbon", soluble organic fraction (SOF) and sulfates. Composition of particulates was studied with the bus engine and the TDI vehicle. Using bioesters in the bus engine effectively reduced the "black carbon" portion, while the SOF was higher with bioesters than with the base fuel. However, this SOF portion can be reduced by using an oxidation catalyst. Altogether, significant PM reductions can be achieved when combining bioester fuels and an oxidation catalyst.

Aftertreatment devices, which include an oxidation element (oxidation catalyst and CRT pariculate trap), promote the generation of sulfate from fuel sulfur. In this respect the low-sulfur bioesters are advantageous. Differences in sulfate formation were seen as sulfur content of fuel varied both with the oxidation

catalyst and with the CRT catalyst/trap. However, particulate emissions with CRT were extremely low with all fuels containing less than 50 ppm sulfur. The particulates of the TDI vehicle were "dry" (low SOF portion) for all fuels, and no significant differences between the fuels were observed regarding SOF or sulfates.

A slight reduction in PAH emissions (particulate SOF and semivolatile phase) was observed for the bus engine without catalyst when 30% ester blends were compared with the EN590 fuel. The reduction was significant for neat esters. However, the 30% RME blend did not give benefit regarding PAH emissions when compared to the RFD fuel. The EtDI fuel did not result in lower PAH emissions than the EN590 fuel. The PAH emission level was so low in the tests with aftertreatment devices that no effect of fuel was seen. The same applies to catalyst equipped Audi TDI vehicle, although some indications of lower particulate PAH emissions for esters than for the EN590 fuel were seen.

Mutagenicity of particulates (SOF) was studied using the Ames test with the bus engine. Neat esters reduced the mutagenicity of particulate SOF compared to the EN590 fuel in the tests without catalyst. The effects of the 30% ester blends and EtDI fuel were not significant.

The Ames results with oxidation catalyst were low. The oxidation catalyst significantly reduced mutagenicity of particulate SOF, except for RFD and RFD/RME30 fuels, which had low levels regardless of the aftertreatment applied. Even though the mutagenicity level with oxidation catalyst was low, there were some indications that the neat RME gives slightly better results than the EN590 fuel. The CRT catalyst/trap gave no significant benefits regarding mutagenicity of particulate SOF compared to the tests without catalyst. This might be explained by possible formation of nitro-PAH compounds.

Particle size distribution was studied with the bus engine (without catalyst). RME resulted in a lower mass of particulates in the main peak area (around 0.1 µm) on particulate mass distribution curve than EN590 or RFD fuels. The number of particles in nucleation mode (lower than 56 nm) was lower for the RME fuel than for the EN590 fuel. However, the lowest number of particles in that range was observed for the RFD fuel.

The effect of esters on formaldehyde emission was not significant with the bus and the tractor engine, while an increase was observed with the TDI vehicle.

Individual hydrocarbons were analysed in the tests with the TDI vehicle. All $C_1$-$C_8$ hydrocarbons were below the detection limit, except for methane and aromatic compounds. The sum of benzene, toluene and xylenes was lower with low-aromatic fuels (bioesters, RFD) than with the EN590 fuel.

In summary, the general trends for bus and tractor engines were higher $NO_x$, but lower CO, HC and particulate emissions for bioesters than for diesel fuel. The particulates generally seemed to be less harmful for neat bioesters than for hydrocarbon fuels. The changes in emissions were not as significant when 30%

bioester blends were compared with EN590 or RFD as when neat esters were used. No significant differences between the esters were seen in the heavy-duty tests. In the tests with the TDI vehicle the UVOME fuel seemed to give some benefit regarding CO, HC and aldehyde emissions when compared with the RME and SME fuels (perhaps due to high cetane number).

The new TDI light-duty technology showed one interesting result: the $NO_x$ emission was not higher for esters than for hydrocarbon fuels, which often is a problem in heavy-duty engines. The ethanol emulsion fuel gave some emission benefits regarding particulates, but this fuel was not studied as extensively as the other fuels. The hydrated tall oil blend gave worse emission figures than the other fuels, but this is believed to be the result of differences in the base fuel.

*Table 10. Summary of the effect of bioesters on emissions.*

| | HC | CO | $NO_x$ | PM | formald. |
|---|---|---|---|---|---|
| **Volvo (bus) w/o cat** | | | | | |
| 30% ester vs EN | — or ns | — | ns | -18…-24 | ns |
| 100% ester vs EN | — | — | +13 | -60 | ns |
| *30% ester vs RFD* | *—* | *—* | *+7* | *-10* | *ns* |
| *100% ester vs RFD* | *—* | *—* | *+34* | *-47* | *ns* |
| **Volvo (bus) ox. cat** | | | | | |
| 30% ester vs EN | ns | ns | ns | -33…-47 | ns |
| 100% ester vs EN | — | ns | +11 | -82 | ns |
| *30% ester vs RFD* | *ns* | *—* | *+7* | *-26* | *ns* |
| *100% ester vs RFD* | *—* | *ns* | *+29* | *-68* | *ns* |
| **Volvo (bus) CRT** | | | | | |
| *30% ester vs RFD* | *ns* | *ns* | *+7* | *ns* | *ns* |
| **Valmet tractor engine** | | | | | |
| 30% ester vs EN | — | — | +5 | -21 | ns |
| **Audi TDI vehicle, FTP** | | | | | |
| 30% ester vs EN | — | — or ns | ns | -22 | +10…+43 |
| *30% ester vs RFD* | *—* | *—* | *-5* | *-13* | *+16* |

| | PM SOF | "black carbon" | 14 PAHs PM SOF | 14 PAHs semivol. | Ames |
|---|---|---|---|---|---|
| **Volvo (bus) w/o cat** | | | | | |
| 30% ester vs EN | + | — | — | ns | ns |
| 100% ester vs EN | + | — | — — | — — | — |
| *30% ester vs RFD* | *+* | *—* | *ns* | *ns* | *ns* |
| *100% ester vs RFD* | *+* | *—* | *— —* | *ns* | *+* |
| **Volvo (bus) ox. cat** | | | | | |
| 30% ester vs EN | + | — | ns | ns | ns |
| 100% ester vs EN | + | — | ns | ns | ns |
| *30% ester vs RFD* | *—* | *—* | *** | *ns* | *ns* |
| *100% ester vs RFD* | *+* | *—* | *** | *ns* | *ns* |
| **Volvo (bus) CRT** | | | | | |
| *30% ester vs RFD* | *ns* | *ns* | *ns* | *ns* | |
| **Audi TDI vehicle, FTP** | | | | | |
| 30% ester vs EN | ns | — | — | ns | |
| *30% ester vs RFD* | *ns* | *—* | *** | *ns* | |

— reduction in emission  + increase in emission  **ns** = not significant  *) doubtful result   numbers = change-% when ester is compared with base fuel

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