EMISSIONS FROM HEAVY-DUTY ENGINE WITH AND WITHOUT AFTERTREATMENT USING SELECTED BIOFUELS

Aakko, Päivi1*
Nylund, Nils-Olof²
Westerholm, Mårten¹
Marjamäki, Marko²
Moisio, Mikko²
Hillamo, Risto³
Mäkelä, Timo³
¹Technical Research Centre of Finland, Finland; ²Tampere University of Technology, Finland; ³Finnish Meteorological Institute, Finland

KEYWORDS
Heavy-duty, biofuel, emissions, particulate, unregulated

ABSTRACT
The tests were carried out with a Euro 2 emission level Volvo bus engine without a catalyst, with an oxidation catalyst and with a CRT particulate trap. 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 and as neat esters. RME was also blended (30%) into reformulated diesel fuel. The test fuel matrix also included Canadian diesel fuel blended with 10% hydrated tall oil and an emulsion of reformulated diesel and some 15% ethanol.

Compared to hydrocarbon fuels, the bioesters reduced CO and HC emissions in most cases. Adding 30% ester in the European fuel did not affect the NOx emission significantly, whereas neat ester resulted in an increase of around 10% in the NOx emission. The effect of esters on the formaldehyde emission was not significant. The ethanol blend reduced NOx and PM emissions compared with the European grade fuel. Clear reductions in PM emissions were noted with bioesters. Using bioesters effectively reduced the “black carbon” portion of particulate matter. Significant PM reductions were achieved when combining bioester fuels and an oxidation catalyst. The PM emission level with the CRT catalyst/trap was too low to draw conclusions of the effect of fuel.

A reduction in PAH emissions was observed for the bus engine without the catalyst when esters replaced the European grade fuel. The PAH emission level with the aftertreatment devices was so low that no effect of fuel was seen.

Ames test showed that neat esters reduced the mutagenicity of particulate SOF compared to the European grade fuel in the tests with and without oxidation catalyst. The effects of the 30% ester blends and the ethanol blend were not significant. The oxidation catalyst reduced the mutagenicity of particulate SOF, except for reformulated fuel and its blend with RME, which had low levels regardless of the aftertreatment applied. 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 European grade or reformulated fuels. The number of particles below 56 nm was lower for RME than for the European grade fuel. However, the lowest number of particles in that range was observed for the reformulated fuel.

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 esters (VOE) are flexible alternative fuels. Many diesel engines can use them 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 [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. 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 recent studies include only a limited number of fuel alternatives, engine concepts, and extensive analysis of unregulated emissions.

IEA Advanced Motor Fuels Annex XIII "Emission Performance of selected biodiesel fuels” was carried out in 1998 and 1999. 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). Operating Agents of the project were VTT Energy and Oak Ridge National Laboratory. These results are from VTT Energy’s part of the Annex. A summary of the work at both ORNL and VTT will be published later.

ABBREVIATIONS
BLPI Berner low pressure impactor
CRT combination of an oxidation catalyst and a particulate trap (Continuously Regenerating Trap)
DI direct injection
ECE R49 exhaust emission test for heavy-duty engines according to Regulation No. 49 of United Nations
ELPI Electrical Low Pressure Impactor
FTIR Fourier Transform Infrared
GC gas chromatography
HD heavy-duty
IC inter-cooled
MS mass spectrometry
PAH polyaromatic hydrocarbons
PM particulate matter emission
PUF polyurethane foam
SMPS Scanning Mobility Particle Sizer
SO$_4$$_2$ sulfates
SOF soluble organic fraction of particulate matter
TC turbocharged

TEST FUELS
The test fuel matrix included eleven fuels (Table 1). 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 Canadian 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. 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 [27]. The tall oil product was received as a ready blend made from the Canadian diesel fuel. Selected properties of the other test fuels are shown in Table 2.

Table 1. Abbreviations of the test fuels.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Fuel</th>
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<tbody>
<tr>
<td>EN590</td>
<td>European (EN 590) diesel, sulfur content below 500 ppm</td>
</tr>
<tr>
<td>RME100, SME100, UVOME</td>
<td>100 % RME, SME or UVOME</td>
</tr>
<tr>
<td>RME30, SME30, UVOME</td>
<td>EN590 containing 30 % of ester (RME, SME or UVOME)</td>
</tr>
<tr>
<td>RFD</td>
<td>Swedish Environmental Class 1 reformulated diesel</td>
</tr>
<tr>
<td>RFD/RME30</td>
<td>RFD + 30 % RME</td>
</tr>
<tr>
<td>TO10</td>
<td>Canadian diesel fuel + 10 % hydrated tall oil</td>
</tr>
<tr>
<td>EtDI</td>
<td>Emulsion of Swedish Env. Class 1 diesel and some 15% ethanol</td>
</tr>
</tbody>
</table>
Table 2. Selected fuel properties.

<table>
<thead>
<tr>
<th></th>
<th>Density at 15 °C (kg/m³)</th>
<th>Viscosity at 40 °C (mm²/s)</th>
<th>Cloud point (°C)</th>
<th>Sulfur (ppm)</th>
<th>Cetane number</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN590</td>
<td>850</td>
<td>3.1</td>
<td>-9</td>
<td>403</td>
<td>51</td>
</tr>
<tr>
<td>RME30</td>
<td>860</td>
<td>3.4</td>
<td>-7</td>
<td>283</td>
<td>51</td>
</tr>
<tr>
<td>SME30</td>
<td>861</td>
<td>3.3</td>
<td>-8</td>
<td>279</td>
<td>47</td>
</tr>
<tr>
<td>UVOME30</td>
<td>860</td>
<td>3.5</td>
<td>-7</td>
<td>283</td>
<td>51</td>
</tr>
<tr>
<td>TO10</td>
<td>827</td>
<td>1.8</td>
<td>-26</td>
<td>41</td>
<td>45</td>
</tr>
<tr>
<td>RME100</td>
<td>884</td>
<td>4.5</td>
<td>-4</td>
<td>79</td>
<td>55</td>
</tr>
<tr>
<td>SME100</td>
<td>887</td>
<td>4.2</td>
<td>1</td>
<td>82</td>
<td>53</td>
</tr>
<tr>
<td>UVOME</td>
<td>887</td>
<td>4.9</td>
<td>0</td>
<td>92</td>
<td>64</td>
</tr>
<tr>
<td>RFD</td>
<td>815</td>
<td>2.0</td>
<td>-39</td>
<td>&lt;10</td>
<td>54</td>
</tr>
<tr>
<td>RFD/RME30</td>
<td>834</td>
<td>2.5</td>
<td>-22</td>
<td>&lt;20</td>
<td>53</td>
</tr>
</tbody>
</table>

TESTS, ENGINE, AFTERTREATMENT DEVICES AND CYCLE

The were carried out according to ECE R49 cycle with a Euro 2 emission level Volvo DH10A-285 bus engine. 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 measured with FTIR, composition of particulates (soluble organic fraction, sulfates), particulate phase PAH, semivolatile phase PAH, mutagenicity with Ames test, selected particulate size distribution measurements.

The Volvo DH10A is a Euro 2 emission level direct-injection 9.6 litre bus engine with an electronically controlled mechanical fuel pump (Table 3). 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 oxidation catalyst tolerate fuel sulfur up to 500 ppm. The CRT requires a low-sulfur fuel below 50 ppm of sulfur.

Table 3. Data on the test engine.

<table>
<thead>
<tr>
<th></th>
<th>Volvo DH10A-285</th>
</tr>
</thead>
<tbody>
<tr>
<td>application</td>
<td>city bus</td>
</tr>
<tr>
<td>combustion system</td>
<td>direct injection</td>
</tr>
<tr>
<td>charge system</td>
<td>TC, IC</td>
</tr>
<tr>
<td>injection pump</td>
<td>in-line pump</td>
</tr>
<tr>
<td>control</td>
<td>semi-electronic</td>
</tr>
<tr>
<td>number of cyl.</td>
<td>6</td>
</tr>
<tr>
<td>displacement (l)</td>
<td>9.6</td>
</tr>
<tr>
<td>maximum power (kW)</td>
<td>210</td>
</tr>
<tr>
<td>rated speed (rpm)</td>
<td>2000</td>
</tr>
<tr>
<td>max. torque (Nm)</td>
<td>1200</td>
</tr>
<tr>
<td>intermediate speed (rpm)</td>
<td>1450</td>
</tr>
<tr>
<td>aftertreatment</td>
<td>no / ox. cat / CRT</td>
</tr>
</tbody>
</table>

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.

TEST FACILITIES AND ANALYTICAL METHODS

All equipment used for measuring the regulated emissions (CO, HC, NOₓ and particulates) in the heavy-duty tests conform to the specifications for measurement systems given in Annex 4 of ECE Regulation No. 49/02. 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 ∅ 70 mm filters. Semivolatiles were sampled with polyuretane foam plugs (∅ 47 mm, height 5 cm) located after the particulate filter of the MDT 474.

An on-line Fourier Transformation Infra-Red (FTIR) system (SESAM II Fast, manufactured by Siemens AG, FRG) was used to measure more than 20 exhaust components at one second time interval. However, with diesel exhaust gas the
The NOx emission level ranged generally from 5 - 7 g/kWh (Figure 1). The engine stability tests showed that the NOx emission increased in between the testing periods of different aftertreatment alternatives. Hence, no conclusions of the effect of the CRT device on NOx should be done. This does not 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 with and without an oxidation catalyst the change in NOx 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 NOx emission of almost 8%. The RME100 and SME100 fuels resulted in a some 13% higher NOx emission level than the EN590 base fuel. The fuel containing hydrated tall oil and EtDI fuel reduced the NOx emission. The EN590 fuel was not tested with the CRT (too high sulfur content). Thus, the difference between the results with these two bacteria strains indicates the role of nitrated PAH compounds on mutagenicity.

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 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 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 analysis 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. These measurements were carried out with the Volvo engine without catalyst using the test fuels EN590, RFD, EN590 fuel containing 30% RME (RME30) and RME100 on load mode 5 (intermediate speed, 75% load) of the ECE R49 test. The sampling was made close to the point where the total particulate sample is taken in the standardised method. The raw exhaust gas was diluted with MDT gas using dilution ratio 11. The BLPI measurements were carried out by the Finnish Meteorological Institute and the SMPS and ELPI measurements by the Tampere University of Technology.

NOx, HC AND CO EMISSIONS
The NOx emission level ranged generally from 5 - 7 g/kWh (Figure 1). The engine stability tests showed that the NOx emission level of the engine increased in between the testing periods of different aftertreatment alternatives. Hence, no conclusions of the effect of the CRT device on NOx should be done. This does not obscure the comparison of the different test fuels, because the fuel matrixes were run within a short time period with each aftertreatment alternative.

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HC emissions with neat 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. 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 (still about one half of the Euro 2 limit value). It was not relevant to analyse the effect of fuel on HC emissions with the CRT catalyst/trap due to the close-to zero level HC emissions. The oxidation catalyst reduced HC emissions by 70 - 80%. The CRT device was even more effective, the reductions in HC emissions were 94 - 99%.

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 level with the CRT was too low to draw conclusions from possible fuel effect. The oxidation catalyst reduced CO emissions by about 80% and the CRT catalyst/trap by 97 - 99%.

Figure 2 summarizes the effect of bioesters on CO, HC and NOx.
FTIR RESULTS
In the tests without a catalyst, the EtDI fuel resulted in the highest formaldehyde emission level. 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 fuel impact on formaldehyde emissions could not be analysed in the tests with aftertreatment devices due to the low emission levels. The oxidation catalyst reduced formaldehyde emission by about 15 - 40%, and with CRT the reduction ranged 65 - 95%.

The NO2 formation with the aftertreatment devices was high compared to the results without catalyst (more than 2 times higher with the oxidation catalyst and even 9 times higher with the CRT than without catalyst). Strong NO2 formation, especially with the CRT catalyst, results in an unpleasant odour, which can be detected on the road. The formation of laughing gas (N2O) and ammonium (NH3) were below the detection limits of FTIR in all tests.

TOTAL PARTICULATES
PM emissions were 10 - 50% lower for the fuels containing 30% ester than for the base fuels in the tests without a catalyst and with an oxidation catalyst (Figure 3). The reduction of the PM emission with RME100 and SME100 was 60 - 80% compared to the EN590 fuel. TO10 resulted in a higher PM emission than the EN590 fuel in the tests without catalyst, but lower level in the tests with the oxidation catalyst. The EtDI fuel gave lower PM emissions than the EN590 fuel. The oxidation catalyst clearly increased particulate emissions compared to the base case without catalyst for the fuels containing 300 - 400 ppm of sulfur, but the emission still was below the Euro 2 limit (0.15 g/kWh).
The CRT catalyst/trap reduced PM 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.

![PM emission, Volvo engine (ECE R49)](image)

**Figure 3. 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.**

**COMPOSITION OF PARTICULATES**

The compositional analysis of particulates included determination of the soluble organic fraction (SOF) and sulfates. The remaining portion 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 “black carbon” portion reduced clearly as the biocomponent content of fuel increased (Figures 4, 5 and 6). 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. When the oxidation catalyst and neat biofuels were combined, low particulate matter emissions were obtained. Primarily this was a result of the low “black carbon” portion for the bioesters, the effect of the oxidation catalyst on the SOF fraction was less important. The particulates with the biofuels were still after the oxidation catalyst generally more “wet” than with the EN590 fuel (Figure 7).

In the tests without catalyst the share of sulfates and combined water was 10 - 15% with sulfur-containing fuels, but very low with the other fuels. The oxidation catalyst strongly promoted sulfate formation: sulfates and combined water represented 20 - 60% of the particulate matter.
With the CRT device the absolute particulate emission was really low, and thus the absolute emissions of sulfates and SOF were only a fraction of that obtained without catalyst and with oxidation catalyst. However, in relative terms high sulfates and SOF fraction for the RME100 fuel was seen (Figure 8).

![Composition of particulates, Volvo w/o cat (ECE R49)](image)

![Composition of particulates, Volvo with ox. cat (ECE R49)](image)

Figure 4. Composition of particulates as mg/kWh with Volvo engine without catalyst and with oxidation catalyst.

![Soluble organic fraction, SOF](image)

![Others than SOF or sulfates, "Black carbon"](image)

Figure 5. SOF and others than SOF or sulfates vs biocomponent content of fuels.
PAH COMPOUNDS IN PARTICULATE AND SEMIVOLATILE PHASE, AMES TEST RESULTS
The major part of the PAHs was found in the semivolatile phase 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 was more than 60% with the oxidation catalyst for the major part of the fuels (Figure 9). Using the CRT catalyst/trap the level of PAH compounds in the particulates hardly exceeded the detection limit, but the PAH level in the semivolatile phase was roughly the same as with the oxidation catalyst.

The differences between the test fuels were difficult to analyse due to the low PAH emission level of this engine, especially in the tests with catalysts. It seems that the bioesters reduced the PAH emission level when no aftertreatment was used (Figure 10). In the tests without catalyst all fuels containing bioesters resulted in lower particulate and semivolatile phase PAH emissions than the EN590 fuel, especially the RME100 and SME100 fuels. When 30% RME was added to the RFD fuel, only a little benefit was seen regarding the PAH emission. No real benefit in PAH emissions were seen for the EtDI or TO10 fuels compared to the EN590 fuel. With the aftertreatment devices no consistent differences between the fuels were seen.
The results of the Ames test on the particulate SOF fraction are shown in Figure 11. 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.

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. 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.

The oxidation catalyst reduced the mutagenic activity of the particulate SOF fraction with the exception of RFD and RDF/RME30, which already had low mutagenic activity without catalyst. The masses of the samples collected in the CRT tests were not high enough to study mutagenicity with both bacteria strains. No significant changes in mutagenic activity with strain TA98-S9 were observed when the results with and without CRT were compared with each other 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 similar level of mutagenic activity with the CRT catalyst/trap as without aftertreatment.

Figure 12 summarizes the effect of bioesters on total PM, PAHs and mutagenicity tested with Ames.
Figure 10. The effect of fuel on the sum of 14 PAHs with Volvo engine, ECE R49.

Figure 11. Ames test results with Volvo engine, ECE R49 test.
Figure 12. The effect of esters on PM and PAH emissions and on Ames mutagenicity of particulate SOF with Volvo, ECE R49 test.

PARTICLE SIZE DISTRIBUTION MEASUREMENTS
Particle size distributions were measured from the Volvo bus engine without catalyst at ECE R49 load mode 5 using three different instruments, a BLPI impactor, a SMPS instrument and an electric ELPI impactor. The particle number distributions shown in Figures (per cm³) are without correction of the dilution factor (around 11).
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 (Figure 13). 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.

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 14. 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 [30, 31], 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. 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
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 [32].

**Figure 14. ELPI and SMPS number size distributions for different fuels.**

**SUMMARY**

The tests were carried with a Euro 2 emission level Volvo bus engine without a catalyst, with an oxidation catalyst and with a CRT catalyst/trap using eleven test fuels. 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).

Adding 30% ester in the EN590 fuel did not affect the NO\textsubscript{x} emission significantly, whereas neat ester resulted in an increase of around 10%. When 30% ester was blended into the RDF fuel, the NO\textsubscript{x} emission increased by 5…7%. The EtDI fuel resulted in a lower NO\textsubscript{x} emission than the EN590 fuel with the bus engine. Compared to hydrocarbon fuels bioesters reduced CO and HC emissions in most cases. However, the absolute differences were low when aftertreatment devices were used (close to zero emission level). The EtDI fuel resulted in a significant increase in CO and HC emissions. The effect of esters on formaldehyde emission was not significant.

Clear reductions in PM emissions were noted with bioesters. 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 effectively reduced the “black carbon” portion, while the SOF was higher with bioesters than with the base fuel. Significant PM reductions were achieved when combining bioester fuels and an oxidation catalyst. The PM emission level with the CRT catalyst/trap was too low to draw conclusions of the effect of fuel.

Oxidation oxidation catalyst and CRT pariculate trap promoted the generation of sulfate from fuel sulfur. However, particulate emissions with CRT were extremely low.

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.

According to Ames test results the neat esters reduced the mutagenicity of particulate SOF compared to the EN590 fuel in the tests without catalyst. The effect of the 30% ester blends and EtDI fuel was not significant. 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) 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.

In summary, the general trends were higher NOx, 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 different esters were seen in the heavy-duty tests. 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.

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