



Electrofuel Concept of Diesel and Oxygenate Fuels Reduces Engine-Out Emissions

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Abstract

Electrofuels produced from renewable hydrogen (H_2) and captured carbon dioxide (CO_2) can be sustainable and carbon-neutral. Paraffinic electro-diesel (e-diesel) can be produced via Fischer-Tropsch synthesis with fuel properties resembling hydrotreated vegetable oils. Electrofuels can be also oxygenated compounds, such as oxymethylene dimethyl ethers (OMEn), having different chain lengths. We studied emissions using paraffinic diesel mimicking e-diesel and its blend with 10% of OME3-5, which has diesel-type fuel properties, in comparison with normal EN590 diesel fuel. An intensive measurement campaign was performed with a modern diesel engine without exhaust aftertreatment to study the effect of fuel on the engine-out emissions. Measurements with the RMC-C1 cycle included detailed characterization of gaseous, particle and polyaromatic hydrocarbon (PAH) emissions having adverse effects on health and

the environment. In these tests without a diesel particulate filter, the fuel containing the OME3-5 component reduced the black carbon (BC) emissions substantially in comparison with EN590. PM and PAH emissions, as well as the number of non-volatile particle numbers (nvPN), were lower for paraffinic fuel than for the EN590 fuel, and particularly for the OME3-5 blend. As regards gaseous emissions, paraffinic fuel showed lower engine-out NO_x emissions than the EN590 fuel, however, OME3-5 oxygenate did not further increase this NO_x reduction. Higher formaldehyde concentration in the exhaust was found for OME3-5 containing fuel than for the hydrocarbon-only fuels, which can be tackled with an inexpensive oxidation catalyst. In summary, e-diesel type paraffinic fuel reduced the engine-out exhaust emissions from a modern diesel engine substantially, and OME3-5 addition further reduced the most harmful emission species even at a 10% blending level.

Introduction

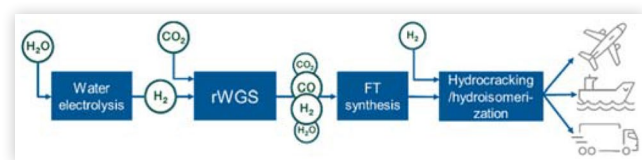
Transport sectors are substantial emitters of greenhouse gases, and hence ambitious targets have been set to cut these emissions to tackle global warming. Electrification is seen as a pathway to reduce emissions from cars, while heavy-duty transport, shipping and aviation are foreseen to be dependent on other types of energy sources in the foreseeable future. If biofuels would cover 20-40% of sustainable liquid and gaseous fuels in 2050, the rest could be covered by electrofuels (e-fuels) produced from hydrogen. When green hydrogen (H_2) is combined with captured carbon dioxide (CO_2), hydrocarbon drop-in fuels would represent sustainable alternatives for fossil fuels. Conversion of renewable electricity to electro-fuels is an increasingly interesting concept potentially enabling the shift from fossil to renewable energy.

Greenhouse gas (GHG) emissions of fuels depend on raw materials and production processes. In RED2, e-fuels are

classified as "renewable fuels of non-biological origin" (RFNBOs). E-fuels will need to meet an emission-saving target of 70%, to be accounted for in the national renewable energy targets. In the JEC study, GHG savings with e-fuels depended on the assumptions made for the emissions of electricity used for electrolysis and origin of the CO_2 , and on the pathways selected to produce e-fuels [1].

Many possible e-fuel chemistries exist, such as e-methane, e-methanol, and e-diesel. E-fuel resembling hydrocarbonaceous diesel fuel, called e-diesel, can be produced from CO_2 and H_2 in a two-step process (Figure 1). CO_2 is first converted to carbon monoxide (CO) in a reverse water-gas shift reaction (RWGS) and the formed synthesis gas (mixture of CO and H_2) reacts to hydrocarbons in Fischer-Tropsch (FT) synthesis [2, 3]. In FT, a distribution of linear hydrocarbons with different chain lengths is formed mainly of paraffins, especially if the cobalt-based catalyst is used in the FT synthesis.

FIGURE 1 Production of e-fuels from CO₂ and H₂ in a two-step process.



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Fuel properties of e-diesel depend to some extent on the FT step and other fractions than diesel (gases, gasoline, wax) are obtained as well always in FT. The primary FT product mainly contains linear paraffins with poor cold properties as diesel fuel. Therefore, catalytic hydroisomerization is typically performed for FT diesel fraction to create isoparaffins and to improve the cold properties. Furthermore, hydrocracking is often applied to increase diesel fraction or more generally middle distillate fraction yield by cracking the wax fraction. The diesel component produced by the gas-to-liquid (GTL) process is very similar to the diesel produced from CO₂ and H₂ by RWGS and FT synthesis and it consists as well of paraffinic compounds. The paraffinic diesel fuel obtained from FT synthesis resembles also the renewable diesel fuel produced by hydrotreatment of vegetable oils or animal fats (HVO), which is known to consist of paraffinic compounds.

Generally, paraffinic diesel fuels are known as clean-burning and suitable for diesel engines at high blending ratios. Paraffinic fuels typically reduce pollutants, e.g. nitrogen oxides (NO_x) and particulate matter (PM). [3, 4, 5, 6]. The addition of oxygenates in diesel fuel can reduce emissions, and these oxygenates could also be e-fuels produced from hydrogen and CO₂. Some oxygenated components are known to be suitable for blending with diesel fuel, such as fatty acid methyl ester (FAME) and di-n-pentyl ether (DNPE) [4, 7, 8]. Oxymethylene dimethyl ethers (OMEn, methylal, dimethoxymethane) have been studied as diesel fuel components, and recently attention has been given to its production by the e-fuel principles.

OMEn has a molecular structure (H₃C-O-(CH₂-O)_n-CH₃) having a high amount of molecular oxygen (42 wt% for OME1, almost 50 wt% for long chain OMEs) [9, 10]. OMEn can be produced from H₂ and CO₂ via methanol, hence, representing e-fuel oxygenate. OME1 produced via methanol can follow formaldehyde route or selective direct oxidation of methanol in the gas phase and reaction of methanol with H₂ and CO₂. In the production of OME1, its purification is challenging due to the formed azeotrope with methanol [11]. Bongartz et al. [11] found reasonable efficiency (73%) of the OME1 production process, although lower than that of e.g. e-methane or e-methanol. Production efficiency can be improved by integrated processes, direct synthesis and other developments. Omari et al. [10] found that the synthesis of OME3-5 demands 14% more hydrogen than a synthesis of OME1 leading to 36% higher final exergy demand. Deutz et al. [12] conducted a life cycle assessment (LCA) showing reductions in pollutant and GHG emissions when OME1 and diesel fuel emissions are compared.

The short-chain OME1 (methylal, DMM) was studied first as a fuel for diesel engines [9], however, longer chain

OMEn molecules are more diesel-like as regards cetane number, viscosity, lubricity, vapour pressure and flash point. OME1 has a high vapour pressure and a low flash point, which is challenging for the control of fuel tank evaporative emissions. The low viscosity is challenging for high-pressure injection systems [10]. The longer-chain OME5 has a challenging freezing point (+18 °C), hence it is mixed with lower-chain OMEn. OME3-5 (<30 wt% OMEn≥5) in the market is reported to have a cold filter plugging point (CFPP) of −18 °C. Omari et al. [10] observed that blending 10% of OME3-5 with paraffinic diesel fuel showed a cloud point of +5 °C. The density difference between paraffinic diesel and OME3-5 is high. Volumetric LHV is almost independent of the OME's chain length since density compensates for differences. Omari et al. [10] ensured the OME compatibility of the fuel system by replacing sealing elements made of nitrile butadiene rubber (NBR) or Fluorine Kautschuk Material (FKM) to polytetrafluoroethylene (PTFE) and conventional fuel hoses with stainless steel or PTFE tubes (no modifications to the fuel injector).

Exhaust PM emission from a single-cylinder research engine was reduced by more than 80% with a 35 vol% of OME1 blend when compared with diesel fuel in a study by Omari et al. [13]. The PM reduction was deemed to be due to OME1's high oxygen content, lack of C-C bonds, low aromatic content, higher volatility and lower reactivity. They also observed reduced HC and CO emissions and exhaust gas temperatures, while thermodynamic efficiency increased up to 2%, respectively. Other studies with single-cylinder engines have reported reduced NO_x and soot emissions (even by 43% and 75%) by using OME1 [9] and soot-free combustion with OME3-5 [10]. The latter study covered blends of OME1, OME2, OME3, OME4, OME5, OME3-5 with diesel fuel at a blending ratio of 35 vol% (approx. 23.5% diesel fuel energy substitution) showing reduced HC and CO (up to 90%) emissions, increased efficiency (up to +3%) and lowered exhaust gas temperature (up to −70 °C). Pure OME3-5 improved the NO_x-PM trade-off, which would allow a simplified aftertreatment system and further reductions in the NO_x emission. The particle number (PN) concentration reduced with OME3-5 and size distribution shifted towards lower particle diameters (peak at 10 nm), which may be challenging for the present particulate filters. Small particles may be due to the fuel or motor oil. Increased formaldehyde emission at lower loads was observed with OME. At higher loads, formaldehyde emissions were lower along with more complete combustion. Reduced methane emissions were explained by the favourable in-cylinder oxidation with OME. [10]

In this work, e-diesel and its combination with e-oxygenate were studied, since these could provide clean liquid e-fuels for diesel engines that are anticipated to remain in use in the heavy-duty, marine and aviation sectors, at least, while cars are electrifying. OMEn was used as e-oxygenate to bring oxygen even in the least accessible regions of combustion. Of many OME ethers having different chain lengths, we selected OME3-5 ether to be blended with paraffinic fuel (HVO) resembling e-fuel diesel. Engine-out emissions from a modern heavy-duty diesel engine were comprehensively studied with three fuels: European grade diesel, paraffinic fuel and its 10% OME3-5 blend. Emission measurements studied covered gases, non-volatile particles, semivolatile compounds (SVC). Measurements were carried out by the VTT Technical

TABLE 1 Characteristics of AGCO 44HD engine.

Displaced volume, L	4.4
Maximum power, kW	112 @ 1900 min ⁻¹
Maximum torque, Nm	650 @ 1500 min ⁻¹
Stroke, mm	120
Bore, mm	108
Number of cylinders	4
Emission standard	Stage V, here without aftertreatment

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Research Centre of Finland, Tampere University (TAU) and the Finnish Meteorological Institute (FMI).

Experimental

Engine, Motor Oil, Test Cycle

The AGCO 44HD Stage V engine, model year 2021, however, without aftertreatment, was installed at VTT for the measurements (Table 1). Engine and dynamometer parameters were logged at 1 Hz time resolution. The motor oil was Shell Rimula R5 LE 10W-40. After the motor oil change, the engine was running-in for a period of more than 50 hours with EN590 fuel (a different batch than the test fuel).

The motor oil sample taken before and after the measurement campaign was in normal condition. The acid number had decreased to some extent, while wear metal, water and soot concentrations were normal. Silicon in oil-soluble form was 44 ppm.

Fuels Fuels studied included European grade diesel fuel (EN590 B0, without fatty acid methyl esters), paraffinic HVO resembling e-diesel and its blend with the oxygenated component. From different oxymethylene ethers, OME3-5 was selected for the measurements based on its fuel properties resembling diesel fuel. OME3-5 contains ether chain H₃C-O-(CH₂O)_n-CH₃, where n=3...5. OME3-5 was purchased from ASG GmbH. The following abbreviations are used for fuels:

- EN590 B0 = European grade diesel fuel
- Paraf = Paraffinic renewable HVO diesel fuel
- Paraf+OME = Paraffinic HVO fuel + 10% OME3-5

The blending of OME3-5 with paraffinic fuel was carried out by VTT. The final blending ratio of OME3-5 was 10.6 vol% according weighing and verification by the densities of the final blend and blending components. Selected fuel properties of EN590, Paraf and OME3-5 are shown in Table 2. A more extensive set of analysed fuel properties and calculated properties of a blend are shown in Appendix 1. Safety aspects of OME3-5, which is not a common fuel component, were screened. The material safety data sheet states that the product is not classified as hazardous and for example, first aid measures are conventional (i.e. fresh air, washing with water). The product does not belong to dangerous goods in the sense of transport regulations referred to.

TABLE 2 Selected fuel properties of OME3-5, EN590 and Paraf.

Property	Unit	OME3-5 ^a	EN590	Paraf
Density 15 °C	kg/m ³	1067.1	825.1	780.7
Flash point	°C	69	60	69
Kin. Viscosity 40 °C	mm ² /s	1.2	2.0	3.0
HFRR	µm	410	380	294
Cetane Number / IQT		73.2/-	-/53.4	-/71.2
Sulfur content	mg/kg	<0.5	6.3	<1
Total aromatics	wt%	-	16.1	0.4
CFPP	°C	-24		-40
Lower Heating Value	MJ/kg	19.2	43.0	43.7
Carbon content	%(m/m)	43.8	86.1	84.8
Hydrogen content	%(m/m)	8.68	13.9	15.2
Oxygen content	%(m/m)	42.6	-	-

OME3-5 contained the stability additive.

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Test Procedure

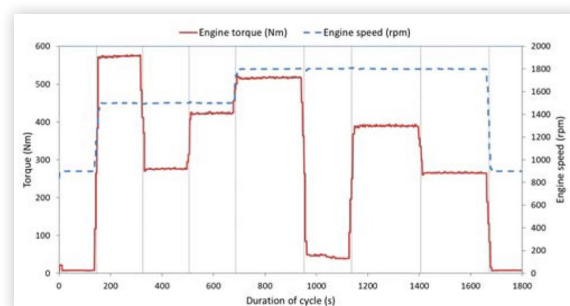
The measurement cycle was RMC-C1 (1800s, 30min, Figure 2). The running-in period after fuel change was at least one hour. Each morning and after the engine stop warm-up periods were included.

A comparison of different fuels is relevant only if the same loads are used for all fuels. Hence, the maximum load achievable with all fuels was used to calculate the load modes of the RMC-C1 cycle, and hence torque was the same for all fuels in each load mode.

Engine dynamometer logging recorded engine speed and torque, inlet airflow (kg/h), test cell temperature and humidity. Engine's electronic control unit (ECU) data was logged, for example, fuel consumption. The feasibility of ECU for accurate fuel consumption measurement has not been studied for oxygen-containing fuels. For the NO_x mass emission calculations (per kWh), correction factors based on test cell humidity and temperature were used.

Test Set-Up and Instruments

Emissions measured included a selection of regulated and non-regulated gaseous emissions, total particle concentrations (i.e. non-volatiles and semivolatiles), and non-volatile particle

FIGURE 2 The RMC-C1 cycle used in the measurement campaign.

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concentration (i.e. volatiles are removed). Black carbon, PM composition and other chemical analyses were also included in the comprehensive emission matrix.

The test set-up is illustrated in Figure 3. Gaseous emissions were measured continuously, online, with two multigas analysers: a) Horiba PG-250 for CO₂, CO, NO_x and O₂ from the raw, dry, exhaust. Principle for NO_x was chemiluminescence (CLD), for CO, CO₂ nondispersive infrared (NDIR), and for O₂ paramagnetic cell. b) FTIR Gasmet DX-4000 for more than 10 gaseous compounds, including NO_x, NO₂, nitrous oxide (N₂O), ammonia (NH₃), CO₂, CO and HC, from raw exhaust gas at a temperature of 190 °C. Concentrations measured with the FTIR are given at 273.15 K. Additionally, multigas analysis by the gas chromatograph from Tedlar bags (diluted, wet exhaust) covered C1-C8 hydrocarbons. In addition to GC, VOCUS instrument was used to analyse concentrations of benzene, toluene, -xylene, 1,3,5-trimethylbenzene, naphthalene and 1,2,4-trichlorobenzene. GC is capable to detect lower concentrations of hydrocarbons than FTIR, while VOCUS is capable to analyse lower concentrations than GC. Aldehydes from the diluted, wet exhaust, collected by 2,4-dinitrophenylhydrazine (DNPH) cartridges, were measured by high-performance liquid chromatography (HPLC).

PM mass emissions were measured from diluted, wet exhaust using Smart Sampler for the dilution of exhaust and collection of samples. Filter diameter was 47 mm otherwise,

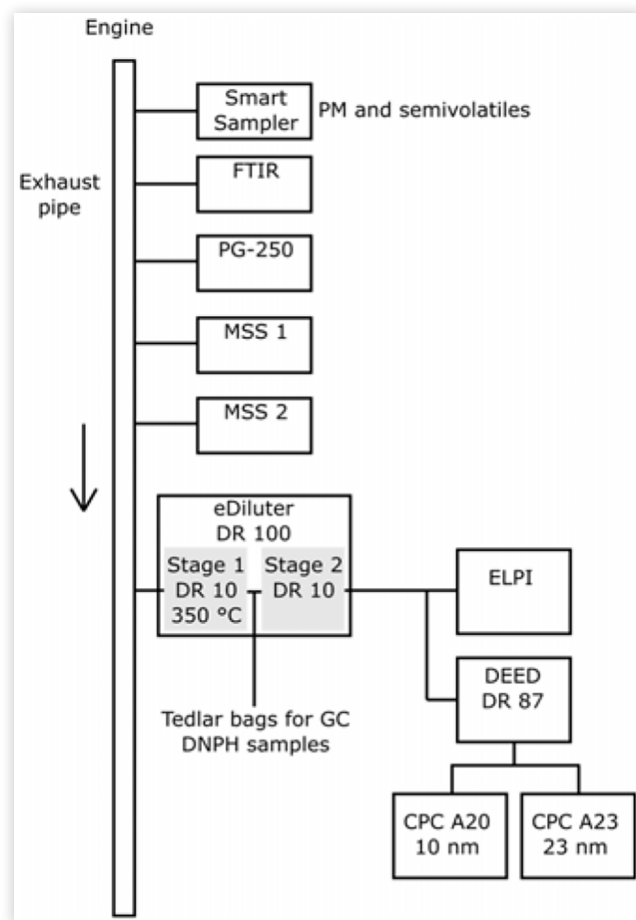
except 70 mm when SVCs were also sampled. Sampling times were 10 min and 30 min, respectively. Diluted exhaust flow was always 60.3 lpm (STP), and hence filter face velocity varied. Filter material was TX40 for PM mass emissions and quartz for elemental carbon (EC) and organic carbon (OC) by thermal-optical analysis (TOA), which was analysed with Sunset instruments. SVCs were collected on AttractSPE™ Disks (HLB), which were located after primary PM filters (TX40, diameter 70mm). PAHs from PM and SVC samples were analysed by Service provider MetropoliLab Oy.

BC was measured with two AVL Micro Soot Sensor (MSS) instruments. The MSS follows the photoacoustic spectroscopy principle. The MSS is calibrated using elemental carbon (EC), which is a proxy of BC, although measurement principles are different (ref). The MSS consists of a sensor unit and a conditioning unit for dilution. The MSS was measuring at 1 Hz. AVL MSS: heated line is 2 m, 52 °C, 3.8 lpm, residence time ~ 1.5, dilution ratio (DR) spec 2-20 (DRs of 10 and 20 used), 1 µg/m³-1000 mg/m³, Rise time <1 s, sensitivity 5 µg/m³.

Non-volatile particle number (nvPN10 and nvPN23) measurements were conducted from diluted, wet exhaust after eDiluter (Dekati Oy) and DEED (Dekati Oy) by condensation particle counters (CPCs). In eDiluter, DR was 100 and a dilution temperature of 350 °C was used. The eDiluter was followed by DEED with a DR of 87. Total DR was 8700. In the DEED, the dilution air temperature was 350 °C and the evaporation tube temperature was 450 °C. After the DEED, particle number concentrations were measured with CPC A20 (Airmodus Oy) in PN10 measurements and CPC A23 in PN23 measurements. The A20 CPC cut-off diameter had been set by the manufacturer to 10 nm.

The size distribution of non-volatile particles was measured continuously with an electrical low-pressure impactor (ELPI, Dekati Oy). The ELPI utilized a filter stage (8 nm) and sintered collection plates. ELPI sampled from the outlet of the eDiluter, which evaporated volatile compounds from particles. The eDiluter was the same unit with the same set-up as in the nvPN measurements. The DR was 100 and with dilution air setting to 350 °C in ELPI measurements.

FIGURE 3 Measurement set-up.

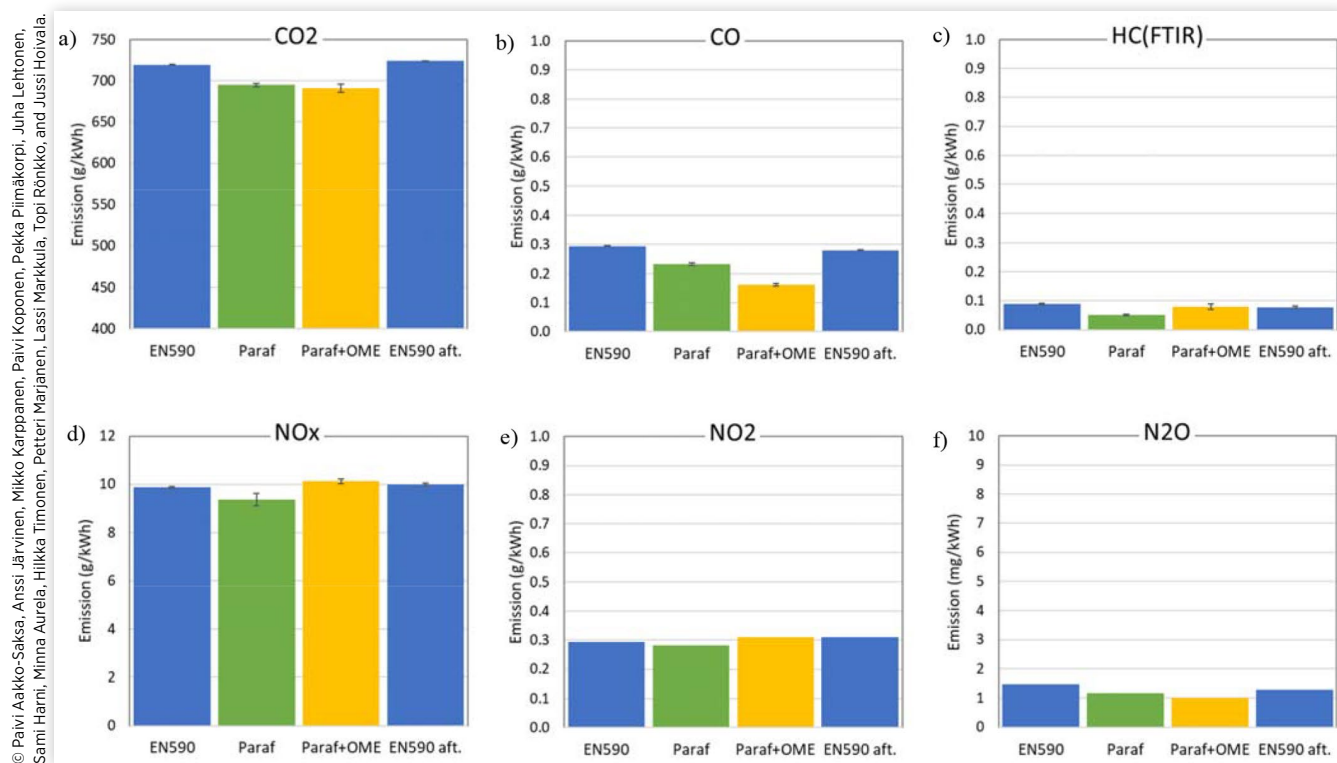


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Results

Gaseous Emissions

CO₂ is a product of the complete combustion of carbon-containing compounds in fuel, while CO and HC are products of incomplete combustion. The completeness of combustion is affected by many fuel properties, such as the heating value and oxygen content of the fuel. Theoretically, differences between carbon to hydrogen (C/H) ratios of fuels are reflected in the sum of carbonaceous emissions (CO₂, CO and HC). For the three fuels tested, the EN590 fuel had the highest aromatic content and hence, the highest C/H-ratio and also the highest CO₂, CO and HC emissions (Figure 4a-c). Paraffinic fuel and OME3-5 addition seemed to improve the efficiency of combustion based on lower HC and CO emissions than those obtained with EN590. Notably, paraffinic fuel had a lower C/H ratio

FIGURE 4 a) CO₂ b) CO c) HC d) NO_x e) NO₂ and f) N₂O mass emissions (per kWh) over the RMC-C1 cycle.

than EN590 fuel and had also lower CO₂ and CO emissions. Combustion may also be assisted by internal oxygen of fuel molecules bringing oxygen into the flame regions that are not easily accessed otherwise. Differences in the HC emissions between fuels were small. The lowest HC emissions were observed for the paraffinic fuel. Typically, also oxygenated components are included in the HC results, and this may explain higher HC emissions for Paraf+OME than for Paraf, which is discussed later. CO₂, CO and HC concentrations for fuels tested in different loads of the RMC-C1 cycle showed the same trends as the mass emissions over the cycle. Differences increased towards higher engine loads in some cases as concerns the CO₂, CO and HC concentrations, while in some cases differences between fuels remained similar regardless of engine load.

NO_x forms from nitrogen present in the intake air. The role of fuel in the NO_x formation is mainly related to its effect on the combustion temperature, spray formation and injection advance. Engine-out NO_x consists mainly of NO and only a few percent is NO₂. N₂O and NH₃ emissions are related to exhaust aftertreatment technologies, while these are not expected to be present in the engine-out emissions from a diesel engine. The benefit of paraffinic fuel in reducing engine-out NO_x emissions was seen (Figure 4d-f), which is in line with the earlier studies [4, 5, 6]. Oxygenate did not show benefit on the NO_x emission. Lower NO₂ emissions were detected for paraffinic fuel and its blend with OME3-5 than for the EN590 fuel. N₂O and NH₃ emissions were low for fuels studied, at the detection limit of FTIR. NO_x, NO₂, N₂O and NH₃ concentrations tested in different loads of the RMC-C1 cycle showed mainly similar patterns as the mass emission

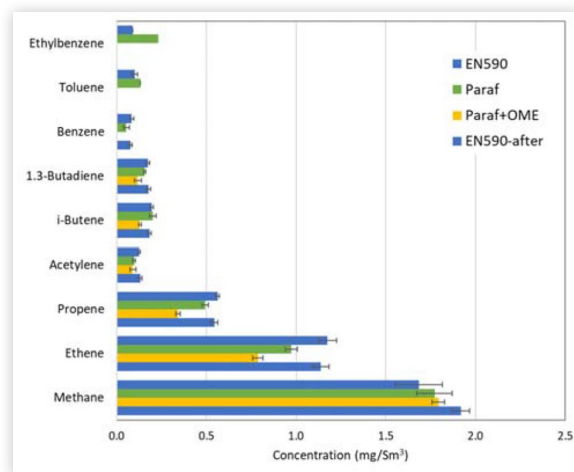
results over the cycle. Differences in emissions between fuels increased towards higher engine loads as concerns the NO_x concentrations, while the NO₂ concentrations showed differences between fuels particularly at the low engine load. Observed N₂O and NH₃ concentrations were always very low.

Individual Hydrocarbons and Aldehydes The harmfulness of different individual hydrocarbons is not equal. For example, some species are toxic or carcinogenic (e.g. benzene), some are greenhouse gases (e.g. methane) and some may contribute to the formation of secondary aerosols (e.g. aromatics). Individual hydrocarbons analysed by gas chromatograph are shown in Figure 5. According to combination of the GC and VOCUS results, aromatic hydrocarbons were present at higher concentrations when using EN590 fuel and the paraffinic fuel was the next, while Paraf+OME induced the lowest levels of aromatics in the exhaust.

The background methane concentration of nitrogen used for the dilution of samples was in some cases high (679 ppb). However, background methane concentrations were not continuously monitored and maybe over-compensated leading to underestimated methane concentrations of samples. Methane, and potentially the other hydrocarbons, were present in the exhaust, especially at low engine loads.

Oxygen-containing compounds in the exhaust are mainly induced by incomplete combustion. Diesel combustion typically results in formaldehyde as the main oxygenated species in the tailpipe exhaust, when the measurements are done without an oxidation catalyst. The OMEn is formed from several carbon-oxygen building blocks, and hence formaldehyde can be expected in the exhaust as a product of incomplete

FIGURE 5 Concentrations of individual hydrocarbons (GC) over the RMC-C1 cycle.



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combustion of OMEn. Indeed, formaldehyde concentrations were higher for OME3-5 containing fuel than for the hydrocarbon-only fuels (Figure 6).

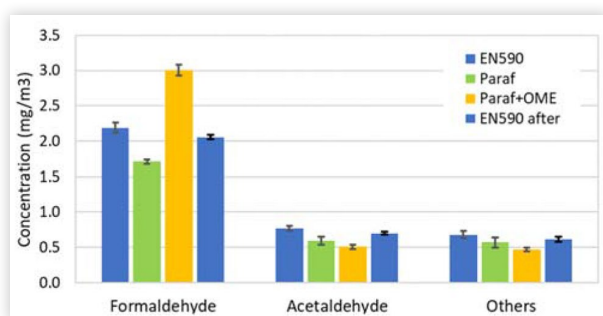
The FTIR data showed that formaldehyde tended to be present at higher concentrations at low engine loads. OME3-5 blended fuel increased formaldehyde concentrations at all engine loads studied, however, an oxidation catalyst is capable of removing formaldehyde from exhaust efficiently.

PM, BC and PAHs in Engine-Out “tailpipe” Total particulate matter was reduced when changing from EN590 to paraffinic fuel and somewhat more when the OM3-5 component was added to paraffinic fuel (Figure 7). The EN590 fuel resulted in the highest PM concentrations regardless of the different sampling conditions used.

The effect of OME3-5 was particularly drastic when evaluating the black carbon emissions and this deduction was consistent over different engine loads (Figure 8a). Practically, BC emissions were reduced to an almost negligible level with a 10% addition of OME3-5.

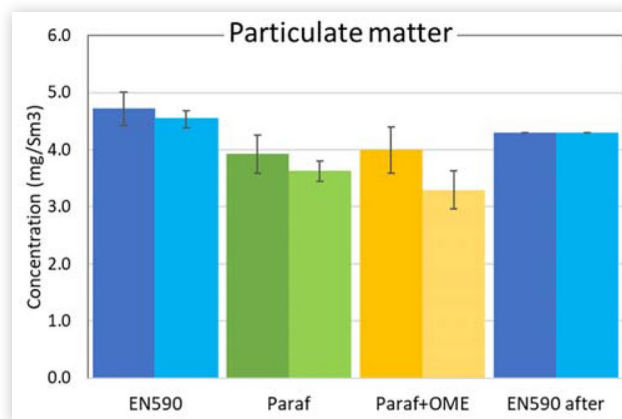
The effect of the paraffinic and OME3-5 blend on the black carbon emission is confirmed by the elemental carbon (EC) results. A clear decrease in EC concentration is seen when

FIGURE 6 Formaldehyde, acetaldehyde and other aldehydes analysed by HPLC over RMC-C1.



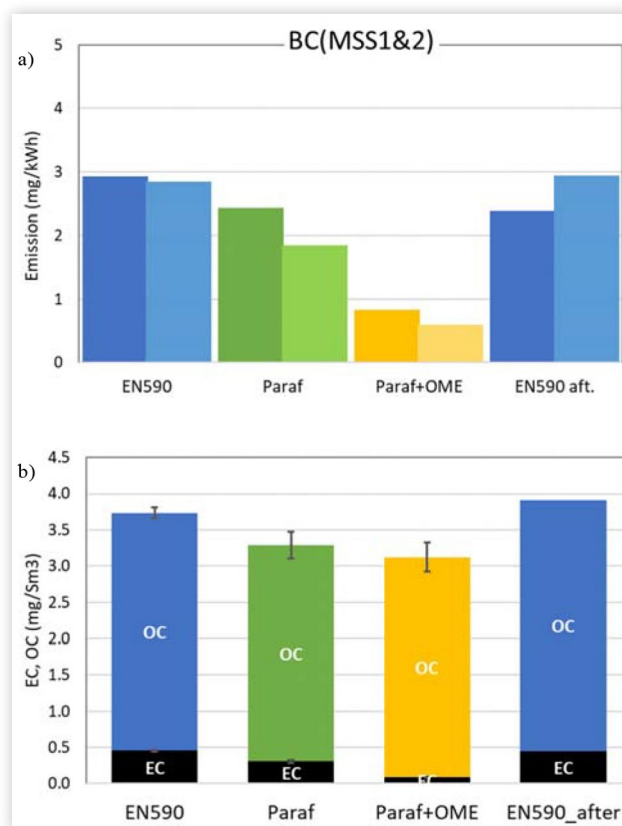
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FIGURE 7 Particulate matter concentrations over RMC-C1 cycle collected on TX40 and quartz filters having a diameter of 47 mm.



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FIGURE 8 Average a) BC emission (mg/kWh) b) EC and OC concentrations (mg/Sm³) for different fuels over RMC-C1. The EN590 was measured twice, at the beginning and after the paraffinic fuel and OME blend measurements.

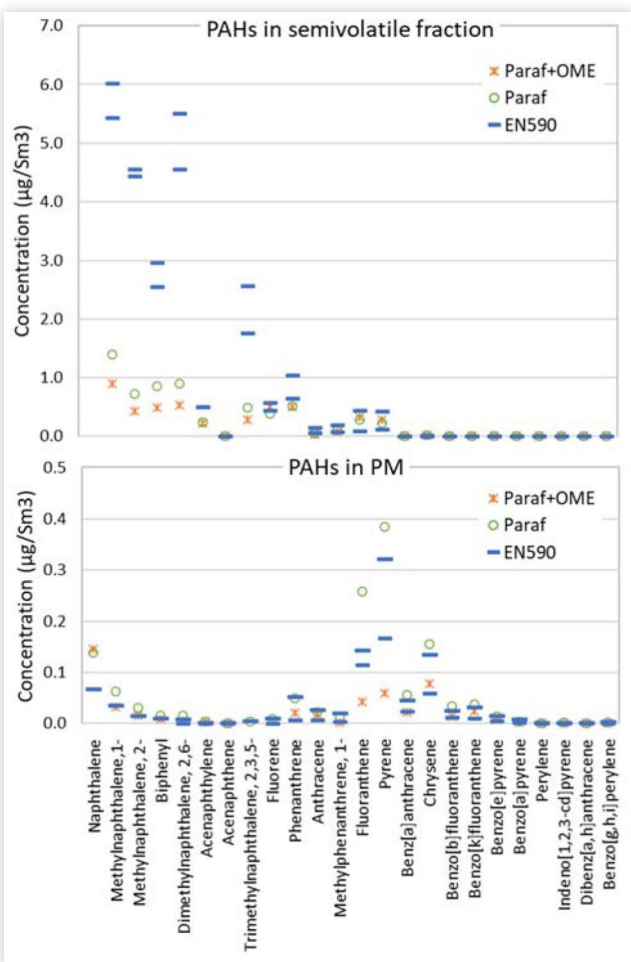


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EN590 fuel is changed to HVO and an even larger decrease when OME is added to HVO. For the organic carbon, the differences between fuels were smaller (Figure 8b).

Particulate matter carries different compounds, also polyaromatic hydrocarbons. Harmful species are carried also by semivolatiles that pass filter collecting PM, especially so since the sampling temperature on the filter is elevated

FIGURE 9 Concentrations of PAH compounds in particulate matter (lower) and semivolatile phase (upper) over the RMC-C1 cycle.



In both cases, OME3-5 addition to paraffinic fuel led to the lowest PAH concentrations, and also paraffinic fuel showed substantially low PAH concentrations in the SVC phase.

Particle Number Emissions The number of non-volatile particles above 23nm (nvPN23) is being regulated today in many regions for cars and vehicles. Anticipated new regulations will address the non-volatile PN10 emissions. Particle number emissions are reduced efficiently with diesel particulate filter, which was not used in this study where the effect of fuel on the engine-out emissions was in focus. Indeed, differences in the nvPN emissions were observed between hydrocarbon-only and fuel containing OME3-5 component (Figure 10a,b). nvPN23 emission when using the OME3-5 component was only 7.9×10^{12} #/kWh, while it was substantially higher for the hydrocarbon fuels. Reduction in particle number emissions is remarkable, although 10% OME3-5 blending in diesel did not reduce the nvPN23 emissions below the current European limit value of 1×10^{12} #/kWh in the tests without diesel particulate filter (DPF). Differences in nvPN23 and nvPN10 concentrations were rather low between EN590 and Paraf fuels, and the same applies to the nvPN concentrations measured with ELPI. In these measurements, sample conditioning was not according to the oncoming PN10 regulation, which may affect the differences between the PN10 and PN23 emissions. However, it was clear that the addition of oxygenate reduced efficiently also the nvPN10 emissions. Low engine-out particle emission level with a 10% oxygenate blend reduces the frequency of the DPF regenerations needed.

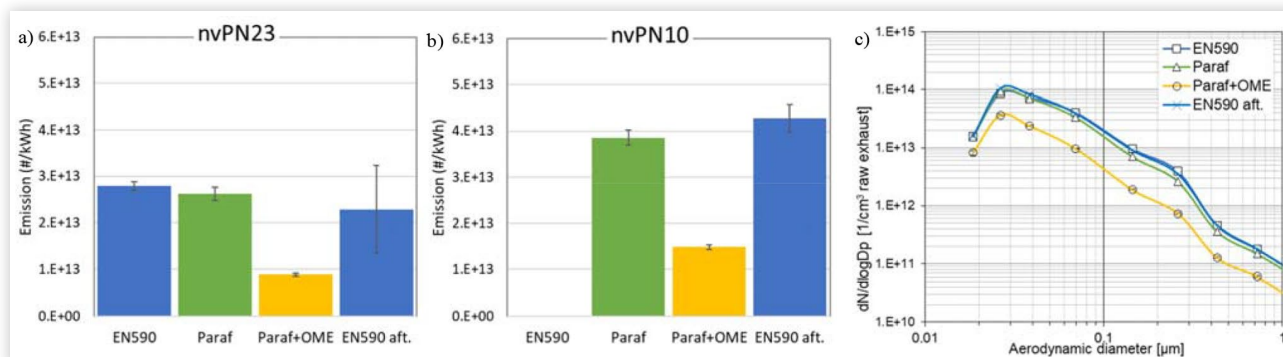
In the tailpipe location where the PN results presented above were sampled, also particle size distribution was measured (Figure 10c). Based on this measurement with the removal of the volatile fraction of particles, the effect of the oxygenated OME3-5 component was seen in all measured particle sizes. Paraffinic fuel also led to lower particle number emissions than the EN590 fuel.

(44–52 °C). A disk for sampling the SVC fraction was used in these measurements and analysis of PAHs was conducted from both PM and SVC samples (Figure 9). PAH profiles of PM and SVC were different as PM contained heavier PAHs, while the SVC fraction contained lighter PAHs at higher concentrations than the PM fraction. Differences between fuels were higher in the SVC fraction than in the PM fraction.

Summary/Conclusions

Transport sectors' greenhouse gas emissions can be reduced by many means, including electrofuels produced from

FIGURE 10 Non-volatile particles a) above 23nm and b) 10nm and c) as particle size distributions (ELPI) for different fuels (EN590, paraf and paraf+OME) over RMC-C1.



renewable hydrogen and captured carbon dioxide. Paraffinic e-diesel produced via Fischer-Tropsch synthesis provides liquid drop-in fuel. Consideration is needed for the tightening emission regulations, for example, cold start emissions apply for the first time for heavy-duty vehicles. In this respect, electrofuels assisting combustion and engine-out emissions are valuable. We studied the capability of the oxymethylene dimethyl ether, OME3-5, as a 10% blend with paraffinic diesel fuel, to reduce engine-out emissions from a modern heavy-duty diesel engine, AGCO 44HD without aftertreatment. OME3-5 has diesel-like fuel properties and can be an e-fuel itself, viz it can be produced from H_2 and CO_2 . Three fuels studied were normal EN590, paraffinic fuel (HVO) mimicking e-diesel and its blend with OME addition. Measurements with RMC-C1 included gaseous emissions, PM with chemical characterisations, black carbon, particle number emissions and size distributions.

The benefit of paraffinic fuel in reducing the engine-out NO_x emissions was clear, while the OME3-5 blend did not further increase this benefit. EN590 fuel had the highest aromatic content and it also induced the highest amount of aromatics in the exhaust. Higher formaldehyde concentration in the exhaust was found for the OME3-5 blend than for the hydrocarbon-only fuels, which is related to the chemical structure of the OME3-5. An inexpensive oxidation catalyst is capable of removing formaldehyde from exhaust efficiently.

The largest effect of the OME3-5 component was seen in the reduction of the black carbon emission, and also PM emissions, in comparison with EN590. BC emission was reduced to an almost negligible level with a 10% addition of OME3-5 in paraffinic fuel, although paraffinic fuel also reduced the BC emission when compared with EN90 fuel. In PM and semi-volatiles, PAH concentrations were lower for paraffinic fuel than for the EN590 fuel, and particularly low for the OME3-5 blend. A decrease in PN concentrations when the EN590 fuel was changed to paraffinic fuel or its blend with OME3-5 was substantial. Altogether, e-diesel type paraffinic fuel reduced the exhaust emissions substantially, and OME3-5 addition further reduced the most harmful emission species even at a 10% blend.

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Definitions/Abbreviations

BC - black carbon
CFPP - cold filter plugging point
CLD - chemiluminescence

CO - carbon monoxide

CO₂ - carbon dioxide

CPC - condensation particle counter

DNPE - di-n-pentyl ether

DNPH - 2,4-dinitrophenyl-hydrazine

DPF - diesel particulate filter

DR - dilution ratio

EC - elemental carbon

ECU - electronic control unit

ELPI - electrical low-pressure impactor

FAME - fatty acid methyl ester

FKM - Fluorine Kautschuk Material

FT - Fischer-Tropsch synthesis

FTIR - Fourier-transform infrared

GHG - greenhouse gas

GTL - gas-to-liquid

H₂ - hydrogen

HC - hydrocarbons

HPLC - high-performance liquid chromatography

HVO - hydrotreated vegetable oils

NBR - nitrile butadiene rubber

NDIR - nondispersive infrared

NH₃ - ammonia

N₂O - nitrous oxide

NO_x - nitrogen oxides

nvPN - non-volatile particle number

OC - organic carbon

OMEn - oxymethylene dimethyl ethers

PAH - polyaromatic hydrocarbons

PM - particulate matter

PTFE - polytetrafluoroethylene

RFNBO - renewable fuels of non-biological origin

RWGS - reverse water-gas shift reaction

SVC - semivolatile compounds

TOA - thermal-optical analysis

Appendix

The properties of used fuels and calculated properties of the “Paraf+OME3-5 (10%)” blend.

Property	Method	Unit	OME3-5	EN590	Paraf	Paraf+OME3-5 (10%), calculated	Note
Density 15 °C	EN ISO 12185	kg/m ³	1067.1	825.1	780.7	809.3	
Density 15 °C	Measured, VTT	kg/m ³	1067		781.3	809.9	see the actual blend below
Flash point	EN ISO 2719	°C	69	60	69	69	Non-linear behaviour
Kin. Viscosity 40 °C	EN ISO 3104	mm ² /s	1.188	1.962	2.995	2.81	
HFRR (Lubricity)	EN ISO 12156-1	µm	410	380	294	306	Non-linear behaviour
Cetane Number	EN ISO 17155		73.2				
Cetane number IQT	ASTM D 6890			53.4	71.2	71.4	Non-linear behaviour
OME 1 content	GC-FID ASG 2506	%	0.01			0.00	
OME 2 content		%	0.13			0.01	
OME 3 content		%	46.79			4.68	
OME 4 content		%	29.76			2.98	
OME 5 content		%	16.95			1.70	
OME 6 content		%	5.62			0.56	
OME content (OME1-OME6)		%	99.26			9.93	
Sulfur content	EN ISO 20846	mg/kg	<0.5	6.3	<1	<1	
Nitrogen content	DIN 5144	mg/kg	135			na	
Water content	EN ISO 12937	mg/kg	15			na	
Total contamination	EN 12662	mg/kg	<12(3)			<12(3)	Non-linear behaviour
Total aromatics	EN 12916	%(m/m)		16.1	0.4	0.4	
Oxidation stability	EN 16091	min	859.26			na	
Freezing Point of aqueous Antifreeze Solutions	ASTM D 6660	°C	-20.6			na	
CFPP	EN 116	°C	-24		-40	-38.4	Non-linear behaviour
Cloud point	ASTM D 7689			-30	-36.5	na	
Formaldehyde content	ASG 1855	mg/kg	11			1.1	
Amount of trioxane	ASG 2504 GC-FID	mg/kg	169			16.9	
Peroxide number	EN ISO 3960	meq O ₂ /kg	<1			<1	Non-linear behaviour
Acid value	EN 12634	mg KOH/g	0.04			0.0	
Steel corrosion	ISO 7120		no rust			na	
Calorific value, lower	DIN 51900-2	J/g roh	19225			1922.5	
Calorific value, upper	DIN 51900-1	J/g roh	21104			2110.4	
Lower Heating Value	ASTM D 4809	MJ/kg		42.961	43.737	na	
Carbon content	DIN 51732	%(m/m)	43.8	86.1	84.8	80.7	Calc. for HC fuels
Hydrogen content		%(m/m)	8.68	13.9	15.2	14.5	ASTM D5291 for HC fuels
Oxygen content	DIN 51732	%(m/m)	42.6			4.3	
Start of distillation	EN 3405	°C		169.9	207.8	na	
Dist-05	EN 3406	°C		189	251.3	na	
Dist-10	EN 3407	°C		194.9	261.7	na	
Dist-20	EN 3408	°C		204.6	270.6	na	
Dist-30	EN 3409	°C		213.9	275.4	na	
Dist-40	EN 3410	°C		224.2	278.4	na	
Dist-50	EN 3411	°C		234.8	280.7	na	
Dist-60	EN 3412	°C		246	282.9	na	
Dist-70	EN 3413	°C		258.9	285.4	na	
Dist-80	EN 3414	°C		274.2	288.4	na	
Dist-90	EN 3415	°C		294.9	292.6	na	
Dist-95	EN 3416	°C		312.4	297.5	na	
Final boiling point	EN 3417	°C		327.7	311	na	

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