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Renewable Methanol with Ignition Improver Additive for Diesel Engines

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Supporting Information

ABSTRACT: Reduced emissions and environmental burden from shipping are an important aim of tightening emission regulations and ambitious climate change strategy. Renewable methanol produced from biomass or from other renewable sources represents one option to face these challenges. We studied the potential of renewable methanol to offer such benefits in diesel operation in a Scania ethanol engine, which is designed for additized ethanol fuel (ED95) containing ignition improver and lubricity additives. Methanol (MD95) with several types of ignition improver and lubricity additives was studied for use in diesel engines. MD95 fuels were clean-burning, emitting even less gaseous emissions than ED95, particularly when glycerol ethoxylate was used as an ignition improver. Particle mass and number emissions originating from additives in the experimental fuels could be reduced with an oxidation catalyst. Reduced additive dosing in the MD95 fuels was studied with the aid of fuel injection into the intake manifold. Overall, the results showed that the monofuel MD95 concept is a promising solution for smaller vessels equipped with 800−1200 kW engines.

1. INTRODUCTION

Shipping faces major challenges due to the tightening of emission regulations. Sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions are already limited in the Emission Control Areas (ECA) designated by the International Maritime Organization (IMO), and a global limit for the fuel sulfur content of 0.5 wt % will apply in 2020. Limits for black carbon (BC) and methane are anticipated as they absorb solar radiation and thus warm the atmosphere. This is of particular concern in the vulnerable Arctic areas that are warming twice as fast as the global average.[1,2] Actions to prevent climate change motivate a search for carbon-neutral fuels to meet challenging targets, such as to reduce greenhouse gas (GHG) emissions from shipping by at least 50% by 2050, as announced by the IMO in a climate change strategy for shipping in 2018.[3] Methanol and liquefied natural gas (LNG) are regarded as promising marine fuel alternatives for meeting sulfur emission regulations.[4,5] SO_x, NO_x, methane, and BC emissions are low for methanol combustion, and its carbon footprint is low when produced from biomass or from other renewable sources. In Iceland, renewable methanol is produced from geothermal carbon dioxide (CO_2) and renewable hydrogen by Carbon Recycling International (CRI). Other commercial scale renewable methanol production facilities are being operated, although methanol is currently still mostly of fossil origin, produced using natural gas or coal as a feedstock.[6] Methanol was used as a motor fuel already from the 1970s to the mid-1990s, and it accounts for 7−8% of China's transportation fuel pool. In Europe, up to 3 vol % of methanol is permitted in gasoline. Methanol is one of the most common chemicals globally, with a production capacity of about 95 Mt,[7] and its prices are competitive with those of on-road fuels.[8] Furthermore, "raw methanol", containing some water and impurities, is approximately 5−7% less expensive to produce than chemical grade methanol and could be used in combustion engines.[6] Methanol is an interesting option to face the challenges of tightening emission regulations in shipping.

Recent reviews of methanol by Verhelst et al.[9] and Landälv[10] provide an extensive view of methanol as a motor fuel. Methanol is a liquid and therefore compatible with the existing infrastructure with only minor changes. Transport, handling, and storage of methanol are similar to that of gasoline. For the same amount of energy stored, methanol needs more space than diesel fuel due to its lower volumetric energy content.[6,11] Corrosion inhibitors and alcohol compatible materials (e.g., stainless steel, carbon iron, and certain plastics) are needed for methanol use. Lubricants must be chosen and dosed carefully to avoid formation of acids during combustion.[6,8,12,13] Safety concerns for neat methanol relate to its invisible flame and relatively wide flammability limits from 6.7 to 36% (concentrations of vapor in air that can ignite). Methanol has a flashpoint of 12 °C, which is lower than the minimum flashpoint of 60 °C specified for marine fuels by the IMO.[14] For use of methanol in spark-ignited cars, these risks are alleviated by blending gasoline in methanol, although in many

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respects methanol is safer than gasoline: it is more difficult to ignite, burns slower, and produces less heat than gasoline. Methanol vapor is heavier than air, similar to vapors from many other liquid fuels. Methanol fire can be extinguished with water. A particularly good feature of methanol in the marine environment is its biodegradability and short half-life in ground and surface water (from 1 to 6 days). Methanol, similar to gasoline or diesel, is toxic and should not be ingested as 10 mL can cause blindness in humans and 60−100 mL can be fatal. Methanol is also dangerous when absorbed through the skin or inhaled. Methanol is odorless below a concentration of 2000 ppm. Safety protocols for use of methanol as a marine fuel are under development by the IMO. The Stena Germanica ferry and the seven Waterfront Shipping chemical tankers underwent risk assessments pertaining to their methanol installations and were approved for operation, demonstrating that safety is not a barrier. In general, the hazards for alcohol fuels are manageable.[9,15]

The fuel properties of methanol are most suitable for spark-ignition engines that are typical for cars,[8] whereas its properties are not appropriate for conventional compression ignition diesel engines without adaptations. In the past, Caterpillar and Detroit Diesel developed glow plug-equipped heavy-duty engines capable of using methanol or ethanol[16,17] and Volvo introduced a heavy-duty methanol concept for studying the capability of using Cetanox (20%) additive to increase the cetane number (CN) of methanol. For using methanol in the diesel cycle, Haraldson[18] listed options of surface ignition, fumigation, emulsion, ignition improvers (such as Scania's concept), pilot fuel-assisted diesel combustion (dual fuel DF, ignition with a pilot diesel fuel), and premixed combustion (spark plug or pilot fuel ignition).

Several studies are available concerning the dual-fuel methanol concept.[19−21] Wärtsilä has developed a methanol−diesel retrofit concept for marine engines, called GD methanol−diesel, which has the advantage of using diesel as a back-up fuel (used in the Stena Germanica ferry). In this technology, changes in the cylinder heads, fuel injectors, and fuel pumps are needed, as well as a special common rail system and ECU.[18,22] Another engine concept developed by MAN is used in several tankers by Waterfront Shipping.[23,24] Advanced combustion concepts are promising for fuels such as methanol and are intensively researched to improve engine efficiency and to reduce emissions.[25] These concepts typically depend on charge dilution, through air excess and exhaust gas recirculation (EGR), to reduce the combustion temperature below the NO_x formation temperature and to reduce heat losses. Examples of such concepts include homogenous charge compression ignition (HCCI), in which NO_x levels of 0.1 ppm can be achieved, and reactivity controlled compression ignition (RCCI), which uses two fuels.[25] Recently, partially premixed combustion (PPC) was investigated with methanol. PPC uses advanced fuel injection strategies, lean mixtures, and high EGR rates to tailor combustion to specific fuel properties. With methanol PPC, very high indicated efficiencies have been achieved (53%) while emissions can be suppressed to below EURO VI levels without any device for aftertreatment of emissions.[26] Methanol use as an emulsion in diesel has also been studied.[27] One option to use alcohols in a diesel cycle is a concept already commercially available, namely, Scania's engine designed for ethanol with ignition improver and lubricity additive (ED95). This concept has been used since 1985 in over 600 buses supplied by Scania to several countries. The modifications to the diesel engines include an increased compression ratio (28:1), a special fuel injection system, and a catalyst to control aldehyde emissions.[28] This monofuel alcohol engine concept was studied with ethanol ED95 fuels and preliminarily also with methanol using the commercial additives of ED95, by Nylund et al.[29,30]

For diesel fuel, ignition improvers are typically nitrates, for example, 2-ethyl hexyl nitrate (2-EHN), nitrites, and organic peroxides,[31] while the ED95 fuel used in Scania ethanol engines, Etamax D, traditionally contains 92 wt % hydrated ethanol (grade 95%), 5.0 wt % ignition improver [poly(ethylene glycol) (PEG) derivative, Beraid, Akzo Nobel], 2.8 wt % denaturants (2.3 wt % MTBE and 0.5 wt % isobutanol), and corrosion inhibitor additive according to SEKAB.[28,32] For methanol, the cetane improver in the past was Avocet, which consisted originally of poly(ethylene glycol) dinitrate (75−90%), methanol (10−25%), lubricity additive (1.5%), and antioxidant (0.1%).[33] However, Avocet may increase risks for corrosion, explosion, toxicity, insufficient lubricity, and NO_x emissions.[34] 2% Avocet and 7% Beraid has resulted in the same ignition delay as Avocet alone. Patents for methanol use in the diesel cycle have included additives consisting of polyoxyalkylene compounds (US 4,298,352) and nitrocellulose and polyether with ethylene oxide units (US 5,659,335). Additionally, ammonium nitrate has been proposed as a cetane enhancer for methanol, as well as dimethyl ether (DME), PEG nitrate, octyl nitrate, hydrazine, and hydroxylamine nitrate.[33] Cetane improvers proposed for biodiesel and methanol blends covered several nitrates and 2-methoxyethyl ether.[35] Recently, Munsin et al.[34] reported a glycerol ethoxylate (GE) additive to be more practical than PEG as it had better solubility in methanol at subzero temperatures and in engine tests it showed low soot emissions, although NO_x emissions increased. The efficiency of an additive is thought to increase with increasing molar mass as a longer molecular chain offers more sites for creation of radicals (a shorter ignition delay), limited by solubility.[34] In 2015, Akzo Nobel[36] released a patent application defining a methanol-soluble alkylene oxide adduct of glycerol additive as an ignition improver with minor amounts of lubricants (fatty acid ethoxylates, esters, and amides) and corrosion inhibitors (e.g., morpholine, imidazolines) for preferably anhydrous fuel (<1 wt % water). Many types of molecules have been proposed as cetane improvers for alcohols; however, studies on cetane improvers for methanol use in the modern monofuel diesel cycle alcohol engines are sparse.

This work focused on the monofuel diesel cycle methanol MD95 concept in Scania's ethanol engine using different ignition improver additives selected on the basis of literature data and on earlier experiences.[31,37] The work described was carried out as a part of the Sustainable Marine Methanol (SUMMETH) project, which was initiated to advance the development of methanol engines and fuel solutions for smaller marine vessels using propulsion engines with power in the range from 250 to 1200 kW,[38] since the Wärtsilä and MAN methanol diesel concepts (in the Stena Germanica ferry and Waterfront Shipping chemical tankers) are targeted for larger engines. The concepts investigated within the project also included spark-ignited engines and PPC.[26] This paper focuses on the MD95 concept.

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2. MATERIALS AND METHODS

2.1. Chemicals and Fuels. Biomethanol for the tests was purchased from LTU Green Fuels. This biomethanol contained methanol >99.3%, water 0.04 wt %, nonvolatile matter <3 ppm, chloride <0.1 mg L^{-1}, ethanol <0.3 vol %, acetone <30 ppm, and free formaldehyde 0.2 mg kg^{-1}.

Methanol fuels were blended at VTT using the following chemicals and components:

- Additives for improving ignition: (A) Beraid 3555 PEG derivate, (B) diglyme, (C) glycerol ethoxylate, (D) glycerol propoxylate, (E) nitrate (metal salt).
- Esters for improving lubricity: rapeseed oil methyl ester (RME "Est1") and ethyl levulinate ("Est2").
- Other oxygenated components: dry ethanol ("EtOH"), 1-octanol ("OcOH"), di-*n*-pentyl ether (DNPE, "eth"), 2-methyl tetrahydrofuran (MTHF, "oxy").
- Deionized water for adjusting the desired water content of fuel.
- Stability additive: 2,6-di-*tert*-butyl-4-methylphenol (BHT).

For preliminary testing of cetane numbers, 12 fuels were blended (Table 1). Blending components of these fuels covered four ignition improver additives (A, B, C, and D), two esters (est1, est2), and three other oxygenates (alc, eth, oxy). One of the fuels was blended with dry methanol, whereas the other blends contained approximately 5.5 wt % water. Densities and water contents were analyzed prior to the cetane number tests.

The main engine tests were carried out with the ED95 reference and three MD95 candidates: MD-1, MD-2, and MD-3 (Table 2). MD-1 contained additive A (PEG). MD-2 contained ignition improver C (GE) and RME (est1). MD-3 contained ignition improver C, est1, and DNPE ether. Additional intake manifold injection testing with the engine was carried out with MD-4, MD-5, and MD-6 fuels. Of these, MD-4 and MD-5 resembled MD-3 but contained lower concentrations of additives. MD-6 contained additive F. RME (est1) blending component separated at least partially from fuel blends containing 5.5 wt % water, which was not foreseen in the preliminary testing of the solubility and cetane numbers.

ED95 was used as a reference fuel. Typically, this fuel contains 5 wt % Beraid additive, 95% ethanol with 5% water, and 2.8% MTBE. ED95 was commercial grade "RED95" from NEOT.

2.2. Cetane Number Analysis. Ignition characteristics of the fuel blends were studied using a constant volume combustion chamber, Advanced Fuel Ignition Delay Analyzer (AFIDA) by Analytik-Service Gesellschaft mbH (ASG), Germany. AFIDA determines generic cetane numbers of fuels from their ignition delay using reference fuel calibration. The injection system achieves pressures up to 1200 bar. Additionally, the constant volume combustion chamber can be heated up to 1000 K and pressurized up to 50 bar. Therefore, ignition properties of fuels having CN even below 20 or above 100 can be determined.[39] Cetane numbers for ED95 and MD-1, MD-2, MD-3, MD-4, and MD-5 fuels were analyzed later than those for preliminary fuel blends. In the later analyses, cetane number levels decreased due to differences in instrument parameters defined according to the EN 17155 and ASTM D8183 standards.

2.3. Engine and Testing Procedures. *2.3.1. Engine.* Tests were carried out at VTT's engine laboratory with an alcohol engine (diesel cycle): Scania EEV Ethanol DC9 270 hp (details in Table S1, Supporting Information). This is an 8.9 L, 5-cylinder engine with a compression ratio of 28:1, and it has unit injectors and EGR. In normal use, the engine is equipped with an oxidation catalyst, whereas here the focus was on engine-out emissions, and therefore a catalyst was not used. The engine is certified as Euro V and meets EEV emission limits when using ED95 fuel and an oxidation catalyst.

2.3.2. Emission Tests. The European Stationary Cycle (ESC) test cycle consisting of 13 engine loads was used with the constant torque method, i.e., the same loads were used for all fuels (Table S2, Supporting Information). At fuel change, the fuel system was flushed with new fuel and the fuel filters were changed. The engine was warmed by running for 20 min at 50% engine load (438 Nm, 66 kW) at 1440 min^{-1} (abbreviated "B50"). Every ESC cycle was repeated,

Table 1. Methanol Fuel Blends Prepared for Testing Their Cetane Numbers[a]

	M (A)	M (A) dry	M (A10)	M (B)	M (C)	M (D)	M (A) + Est1	M (A) + Est2	M (A) + OcOH	M (A) + eth	M (A) + oxy	M (A) + EtOH
methanol, wt %	95	95	90	95	95	95	90	90	90	90	90	65
ethanol, wt %												30
additive A, wt %	5	5	10				5	5	5	5	5	5
add. B, C, D, wt %				5	5	5						
ester, wt %							5	5				
other, wt %									5	5	5	
water content, wt %	6.0	0.9	5.9	6.1	6.0	6.1	5.8	5.9	5.8	5.9	5.8	6.2
density 15 °C, g cm^{-3}	0.819	0.803	0.826	0.820	0.827	0.825	0.822	0.828	0.820	0.818	0.822	0.819

[a]Est = ester, alc = alcohol, oxy = oxygenate, EtOH = ethanol.

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Table 2. Fuels for Engine Testing

component	ED95	MD-1	MD-2	MD-3	MD-4	MD-5	MD-6
methanol dry, wt %		82.9	84.5	80.5	84.6	88.2	93.0
ethanol dry, wt %	83.0						
additive, wt %	A 11.6	A 11.6	C 5.5	C 5.5	C 4.1	C 2.7	F 1.0
ester 1, wt %			4.5	4.5	3.4	2.2	
ether DNPE, wt %				4.0	3.0	2.0	
water, wt %	5.5	5.5	5.5	5.5	5.0	5.0	6.0
stabilization additive, wt %		0.01	0.01	0.01	0.01	0.01	0.01
calculated							
carbon, wt %	50.0	37.8	38.1	39.6	38.8	37.7	34.9
hydrogen, wt %	12.7	12.3	12.3	12.4	12.4	12.5	12.4
oxygen, wt %	37.4	50.0	49.6	48.1	48.9	49.9	52.9
others, wt %	0	0	0	0	0	0	0.4
analyzed properties							
density, g cm^{-3}	0.828	0.827	0.831	0.830	0.823	0.818	
water, wt %	5.3	5.7	5.6	5.6			
cetane number	9.7	7.6	7.7	8.5	7.7	6.9	
lower heating value, MJ kg^{-1}	24.4	17.5	19.6	20.0			

Table 3. Average Emissions (per kWh) over the ESC Test Cycle for the Fuels Tested[a]

	ED95 n[b] = 4 (g kWh^{-1})	MD-1 n = 2 (g kWh^{-1})	MD-2 n = 2 (g kWh^{-1})	MD-3 n = 2 (g kWh^{-1})	SD[d] (g kWh^{-1})	ED95[a] (ppm)	MD-1[a] (ppm)
carbon monoxide, CO	1.32	0.46	0.51	0.60	±0.03	200	60
total organic gases, TOG	0.55	0.53	0.48	0.56	±0.02		
nitrogen oxides, NO_x	2.3	1.9	1.9	2.0	±0.09	280	214
particulate matter, PM	0.034	0.046	0.085	0.083	±0.004		
carbon dioxide, CO_2	674	648	658	655	±0.05	6.1%	5.8%
methanol, CH_3OH	0.005[c]	0.74	0.74	0.73	±0.08	1	104
ethanol, C_2H_5OH	0.71	0.030	0.036	0.008	±0.07	70	3
formaldehyde, HCHO	0.010[c]	0.010[c]	0.003[c]	0.010[c]	±0.001	1.7	2.1
acetaldehyde, CH_3CHO	0.044	[c]	[c]	[c]	±0.005	4	0
nitrogen dioxide, NO_2	0.25	0.22	0.10	0.12	±0.03	26	23
nitrous oxide, N_2O	[c]	[c]	[c]	[c]		<1	<1
ammonia, NH_3	[c]	[c]	[c]	[c]		<1	<1
methane, CH_4	[c]	[c]	[c]	<0.01		<1	<1
	# kWh^{-1}	# kWh^{-1}	# kWh^{-1}	# kWh^{-1}			
particle number, solid	0.7×10^{14}	0.5×10^{14}	4.7×10^{14}	5.5×10^{14}	$\pm 0.6 \times 10^{14}$		
particle number, total	0.8×10^{15}	1.3×10^{15}	1.3×10^{15}	1.0×10^{15}	$\pm 1.2 \times 10^{14}$		

[a]Examples of concentrations (ppm) for the ED95 and MD-1 are given for comparison. [b]n = number of replicate tests. [c]Below the detection limit (DL) of 50 mg kWh^{-1} (4 ppm) for N_2O and 10 mg kWh^{-1} (2 ppm) for NH_3 and CH_4. DL for methanol, ethanol, formaldehyde, and acetaldehyde appr. 4 ppm (>10 mg kWh^{-1}). [d]Standard deviations calculated from the highest emission result for methanol and ED95 fuels, except for CO, ED95 SD is ±0.05 g kWh^{-1}.

and in between cycles the engine was run for 10 min at B50 engine load. Additional engine loads in addition to B50 were used with 5 min of running, namely, 50% load (384 Nm, 71 kW) at 1770 min^{-1} (C50) and a random engine load of 500 Nm at 1250 min^{-1}. ED95 was run as the first and last fuel to verify stability of the engine during the measurement campaign.

The regulated emissions, carbon monoxide (CO), total hydrocarbons (HC), nitrogen oxides (NO_x), and particulate matter (PM), were measured with instruments meeting the requirements of the European Directive 1999/96/EC. The engine dynamometer was an eddy current Froude Consine AG 400 and the fuel balance was AVL FB 733. Exhaust flow was measured with a full-flow Pierburg CVS 120 WT. Gaseous emissions (CO, HC, NO_x, CO_2) were analyzed using a Pierburg AMA 4000. Methanol, ethanol, formaldehyde, and acetaldehyde emissions were analyzed using an FTIR Gasmet Cr-2000. Particulate matter (PM) emissions were measured using a PS2000 C, and regulated solid, nonvolatile particle number (sPN, >23 nm) emissions using CPC, PN-DEED. Particle number size distributions were measured from a CVS tunnel using an Electrical Low Pressure Impactor ELPI, Dekati Ltd. With the regulated PN method, volatile particles were removed at 350 °C and only particles above 23 nm were detected, whereas with ELPI measurements, all particles above 8 nm were detected (volatile and nonvolatile). A schematic illustration of the measurement system is shown in Figure S1 (Supporting Information). Table 3 shows the HC emission results, which were calculated using exhaust densities for alcohol fuels and interpreted as total organic gases (TOG). The standard deviation for CO, HC/TOG and NO_x, PM, and sPN was below 4%, whereas that for FTIR was approximately 10%.

The concentrations presented were measured at 273.15 °C, 103.25 kPa (unit mg Sm^{-3}).

For selected PM filters, simulated distillation was conducted. For this purpose, filters were extracted with dichloromethane in an ultrasonic bath for 20 min and stabilized overnight, and the extract was concentrated. Simulated distillation was conducted with gas chromatography−mass spectrometry using C8−C40 alkane standard.

2.3.3. Cylinder Pressure Instrumentation. One cylinder of the alcohol engine was equipped with a pressure transducer to measure

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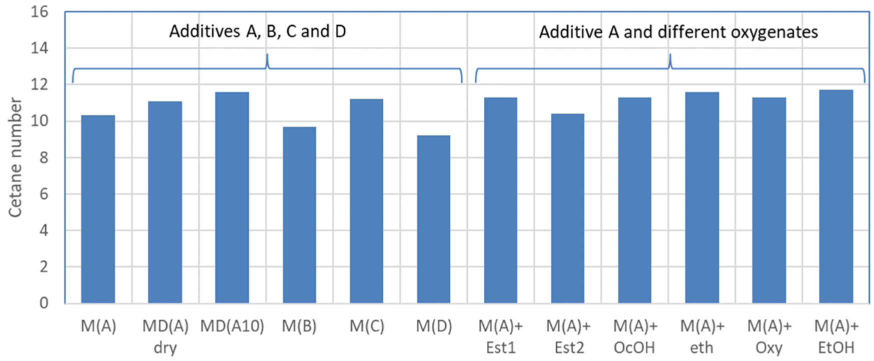

Figure 1. Cetane numbers of the methanol fuel blends determined using a constant volume combustion chamber. Abbreviations of the fuels are presented in Table 1.

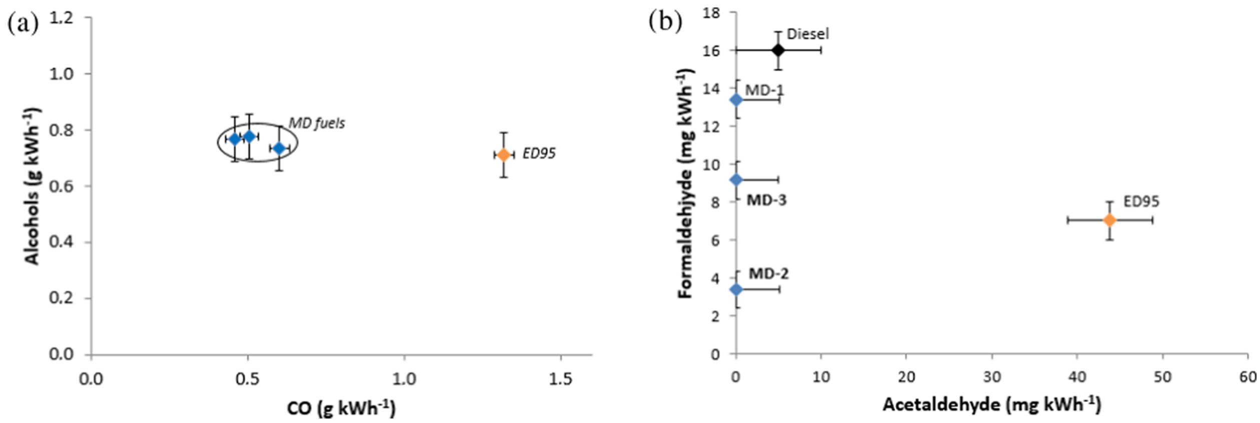

Figure 2. (a) CO and alcohol emissions and (b) formaldehyde and acetaldehyde emissions using MD95 and ED95 fuels, in the ESC test. Error bars represent standard deviation of the results.

cylinder pressure. This system consisted of a Kistler pressure sensor and amplifier controlled with AVL INDICOM software. Pressure data was captured with a 0.1 crank angle degree (CAD) interval. The top dead center (TDC) was defined from the motorized cylinder pressure. Start and duration of injection were determined from the control signal of the unit injector type fuel nozzle. From the captured cylinder pressure data, indicated mean effective pressures (IMEP), heat release rates (HRR), cumulative heat releases (QHR), and ignition delay were calculated.

2.3.4. Intake Manifold Injection Procedure. For two fuels (MD-4 and MD-5), tests were conducted using a special system enabling fuel injection into the intake duct based on a Hestec Harinen 32 electronic control unit (ECU) and Bosch injectors. The system comprised five fuel injectors, a fuel pump, and a simple control system. The system shown in Figure S2 (Supporting Information) is described in detail by Nylund et al.[29] In our study, ED95 was a pilot fuel.

The three load points and their corresponding manifold injection durations were:

- 0 and 2 ms at engine running on idle
- 0, 2, and 4 ms at an engine load of 50 Nm at 900 min^{-1}
- 0, 2, and 5 ms at an engine load of 438 Nm at 1440 min^{-1}

In addition to combustion analysis, gaseous exhaust emissions and energy consumption were measured.

3. RESULTS AND DISCUSSION

3.1. Solubility Testing and Cetane Numbers of Preliminary Blends. The solubility tests of nine multi-component blends showed that all components were fully cosoluble. No phase separation was observed in 3 months after mixing of the components (see Figure S3, Supporting Information).

The ignition characteristics with the new MD95 recipes compared with a blend M(A) simply mimicking the ED95 fuel were studied by using the cetane number analyzed by a constant volume combustion chamber. Twelve methanol fuel blends had cetane numbers from 9.2 to 11.7 (Figure 1), which is lower than the CN of 14.6 for ED95 fuel. Cetane numbers of the MD95 blends were higher when using ignition improver additive C than when using additives A, B, and D. Furthermore, cetane numbers of MD95 blends were higher when using est1, eth, or EtOH than when using OcOH or est2 as the blending components. Additionally, the cetane number of the MD95 blend was higher when the concentration of the cetane improver A was increased from 5 to 10 wt % and when dry methanol was used for blending. On the basis of the solubility and cetane number results, additives A, C, est1, and ether were selected for the MD95 blends for engine tests (Table 2). All fuels prepared for the engine tests had a water content of approximately 5.5 wt %.

3.2. Exhaust Emissions. MD-1, MD-2, and MD-3 fuels operated well in the engine tests over the ESC test cycle, whereas the MD-6 fuel did not ignite in the test engine. Numerical results of the exhaust emissions over the ESC test cycle are presented in Table 3 and results at different engine load points in Table S3 (Supporting Information).

CO emissions for all methanol fuel candidates tested were lower than those for the ED95 fuel (Figure 2a). This indicates more complete combustion for methanol blends than for the ethanol blend. CO emissions were slightly lower for MD-1 and MD-2 than for MD-3. CO emissions from the Scania engine

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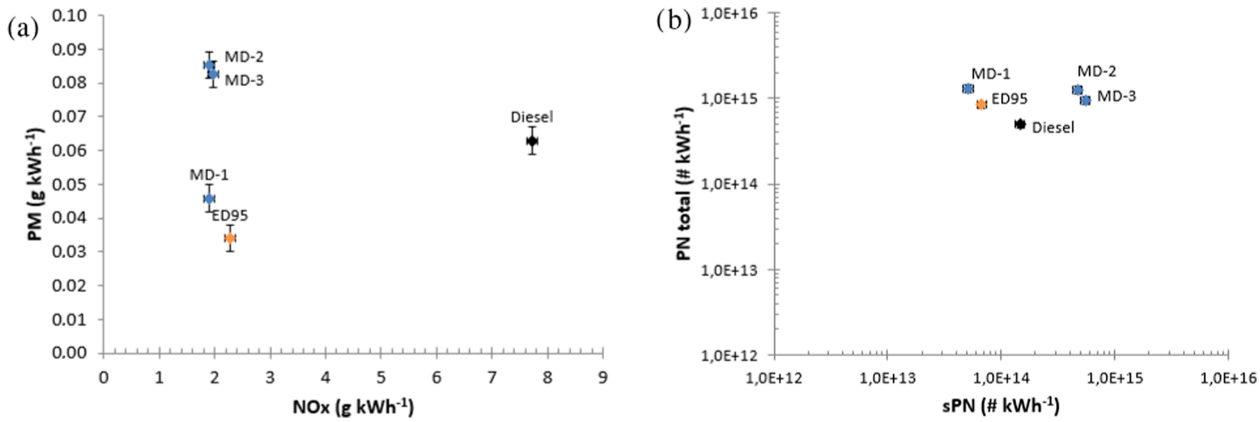

Figure 3. (a) NO_x and PM emissions and (b) total PN and solid PN emissions. MD95 and ED95 fuels in the ESC test cycle. Emissions from a conventional diesel engine are shown as a reference. Error bars represent standard deviation of the results.

were generally low: below the Euro VI limit of 1.5 g kWh^{-1} even without the oxidation catalyst.

No significant differences in the total alcohol emissions were observed between the methanol fuel candidates and ED95; however, the alcohol in the exhaust gas for MD95 was methanol, whereas for ED95 it was ethanol. In the 13 load points of the ESC test, methanol concentrations were at the same level for MD-1 (0.74 g kWh^{-1}, 86−199 mg Sm^{-3}) as the ethanol concentrations for ED95 (0.71 g kWh^{-1}, 97−205 mg Sm^{-3}). For alcohol fuels, TOG emissions are close to the alcohol emissions as organic gases present in the exhaust are mainly unburned alcohols that have an FID response, whereas organic gas emissions from diesel engines are mostly hydrocarbons typically at low concentrations. In these measurements without an oxidation catalyst, organic gas emissions from the Scania ethanol engine were higher than the Euro VI HC limit of 0.13 g kWh^{-1}. These emissions are reduced by the oxidation catalyst incorporated in the Scania ethanol engines, and other solutions such as EGR combined with reforming are also options.[40]

Aldehyde emissions were higher for ED95 than for MD95 fuels, which indicates efficient and clean combustion of the MD95 fuels (Figure 2b). In the 13 load points of the ESC test, the sums of acetaldehyde and formaldehyde concentrations were 2−6 mg Sm^{-3} for MD-1 fuel, whereas higher concentrations were observed for ED95 fuel (acetaldehyde 6−14 mg Sm^{-3}; formaldehyde 1−6 mg m^{-3}). The engine-out acetaldehyde emission level was notable for ED95 but below the detection limit for MD95 fuels. The formaldehyde emissions were at the detection limit with all fuels, and particularly low concentrations were observed for the MD-2 fuel. For engines using diesel fuel, engine-out formaldehyde emissions are often higher than those measured here for alcohol fuels. In Figure 2b, aldehyde emissions from the diesel engine are given as a reference from a previous work[41] and even higher formaldehyde emissions of up to almost 25 mg kWh^{-1} have been reported for diesel engines[42−44] and up to 60 mg km^{-1} for diesel buses and cars.[45,46] Formaldehyde emissions can be efficiently reduced using an oxidation catalyst. Interestingly, the cetane numbers of fuels did not correlate with CO, alcohol, or aldehyde emissions. Cetane numbers of MD-1 and MD-2 fuels were approximately one unit lower than that of MD-3 fuel and two units lower than that of ED95 fuel.

NO_x emissions were slightly lower for the MD95 fuels than for ED95 (Figure 3a). The flame temperature of methanol is lower than that of ethanol (Yao et al.[47] and Figure S9 by Piel,[48] Supporting Information), which may explain this difference. NO_x emissions with alcohol fuels were only a fraction of those obtained with diesel fuel, although higher than the Euro VI limit for NO_x (0.40 g kWh^{-1}).

By default, PM emissions are low when using fuels without carbon−carbon bonds and with higher hydrogen and oxygen contents than traditional diesel fuel.[9] However, the PM emissions with all alcohol fuels studied were relatively high: for MD-2 and MD-3 appr. 0.08−0.09 g kWh^{-1} and for MD-1 and ED95 appr. 0.03−0.05 g kWh^{-1} (cf. the Euro VI PM limit of 0.01 g of kWh^{-1}). However, the material collected on the filters was not black: filters were grayish for ED95 and totally white for the MD95 fuels, indicating that the material on the filters was semivolatile organic matter (not soot). Simulated distillation of the extracted PM filter samples showed that they contained mainly compounds with boiling temperatures in the range of ca. 470−520 °C and some compounds with lower boiling temperatures. On the basis of the mass spectra, the higher boiling fraction is a mixture of fatty acid glyceride type compounds and the lower boiling fraction appeared to consist mainly of aldehydes, fatty acids, and ethoxylate type compounds. The results indicated that PM mass for MD-2 and MD-3 originated mainly from RME ester and for MD-1 from the PEG ignition improver additive. Nonvolatile particle number, sPN (>23 nm), emissions for all tested fuels were 0.6−6 × 10^{14} # kWh^{-1}, which is of the same order of magnitude as engine-out sPN emissions from diesel engines (Figure 3b) and from medium-speed marine diesel engines.[49] sPN emissions were higher for MD-2 and MD-3 fuels containing RME ester than for ED95 and MD-1, and all engine-out sPN emissions were high when compared with the Euro VI limit (8.0 × 10^{11} # kWh^{-1}) that can be met by using diesel particulate filters. Total PN emissions (also including volatile particles) varied from 0.8−1.3 × 10^{15} # kWh^{-1}, an order of magnitude higher than the sPN emissions. The order of fuels for total PN emissions was MD-1 > MD-2 > MD-3 > ED95, although differences between these fuels were not high when considering the uncertainty of the measurement. The particle number size distributions (Figure 4) confirmed that accumulation (soot) mode was very low for alcohol fuels when compared with diesel. All fuels showed a tendency for nucleation, which was due to tunnel dilution favoring the

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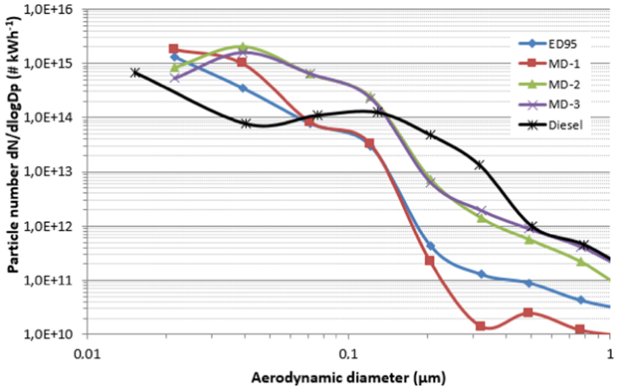

Figure 4. Particle size distributions (volatile and nonvolatile) in the ESC test cycle.

formation of nanoparticles. The nucleation mode was higher for the ED95 and MD-1 fuels than for the MD-2 and MD-3 fuels. The semivolatile type material observed in the PM filters probably explains the relatively high sPN and PN emissions with these alcohol fuels. The chemical structure of the additive molecules affects the ease of removal of such particles. Here, volatile particles (PN) were removed more completely when using ED95 and MD-1 fuels than when using RME-containing MD-2 and MD-3 fuels. Semivolatile matter can usually be removed from the exhaust simply by using an oxidation catalyst,[50] whereas removal of soot is more challenging.

As a summary, MD95 fuels were even cleaner burning than ED95 in the Scania ethanol engine when considering the gaseous emissions. Particularly low aldehyde emissions were observed for MD-2 containing GE ignition improver and RME as additives, although gaseous emissions were also low for MD-3 fuel with a similar composition to MD-2 with the addition of DNPE ether, and for MD-1 and ED95 fuels with PEG ignition improver. By contrast, particle mass and number emissions were higher for MD-2 or MD-3 fuels than for MD-1 and ED95 fuels due to presence of semivolatile particles that mainly originated from RME used as lubrication additive. Semivolatile PM, sPN, and PN emissions could be substantially reduced by the oxidation catalyst integral to the commercial Scania engine.

3.3. Cylinder Pressure Performance. MD95 fuel generated a different cylinder pressure trend as compared with ED95 at 50% engine load at 1440 min^{-1} (B50, Figure 5a), whereas at 50% engine load at 1769 min^{-1} (C50, Figure 5b), the pressures for ED95 and MD95 were rather similar. These differences could be explained by intake air mass flow, as the calculated intake air mass flow is 18.5% higher with ED95 than with MD95 at the B50 load, whereas only 3.2% higher at C50 load. The engine management regulates the intake manifold pressure map in relation to calculated engine load and speed. Engine load is calculated by comparing the injection duration demand with maximum duration. The injection duration is longer for methanol, which has a lower energy density, and the engine management system appears to adjust boost pressure accordingly at some operation points.

The engine operated steadily with MD95 and ED95 fuels. The cylinder pressure deviation was normal (below 1) between fuels. The pressure rise rate (PRR) remained low for all fuels tested, resulting in moderate combustion noise. ED95 generated the highest PRR (Figure 6). The injection duration was shorter for ED95 than for MD95, and the injected fuel energy per crank angle degree was higher. After ignition delay, the rapid ignition and combustion with ED95 caused a higher PRR.

In compression ignited, direct injection applications, combustion duration is somewhat dependent on injection parameters. A longer injection duration therefore results in increased combustion times using MD95 than when using ED95. However, the higher reaction speed combined with more complete mixing of MD95 explains the faster heat release in the late combustion phase (20−40 crank angle degree before the top dead center). The peak QHR was however similar with both fuels (Figure 6). Due to the injector type (pump injector), neither start of injection (SOI) nor end of injection (EOI) could be accurately defined from the control signal. However, indicatively SOI (control signal triggered) was 20.5° for ED95 and 19.4° for MD95 fuels, while respective values for EOI were −0.2 and 3.5°.

The differences in IMEP between ED95 and MD95 fuels were relatively small at 50% load at 1440 min^{-1} (B50) and at 1769 min^{-1} (C50) and 500 Nm at 1250 min^{-1} (Figure 7). Surprisingly, the smallest difference between fuels was observed at 50% load point at 1440 min^{-1}. However, the small variation in IMEP at all loads and fuels was concluded to be normal. Engine efficiency was 38−43% for ED95 and 37−46% for MD95 fuels at the same three load points, as illustrated in Figure 7. Emissions at three load points during cylinder pressure analyses are shown in Table S4 and additional cylinder pressure results in Figures S4−S6 (Supporting Information).

3.4. Intake Manifold Injection Results. The ED95 fuel was injected into the intake manifold in the special tests conducted with MD-4 and MD-5 fuels, which contained less

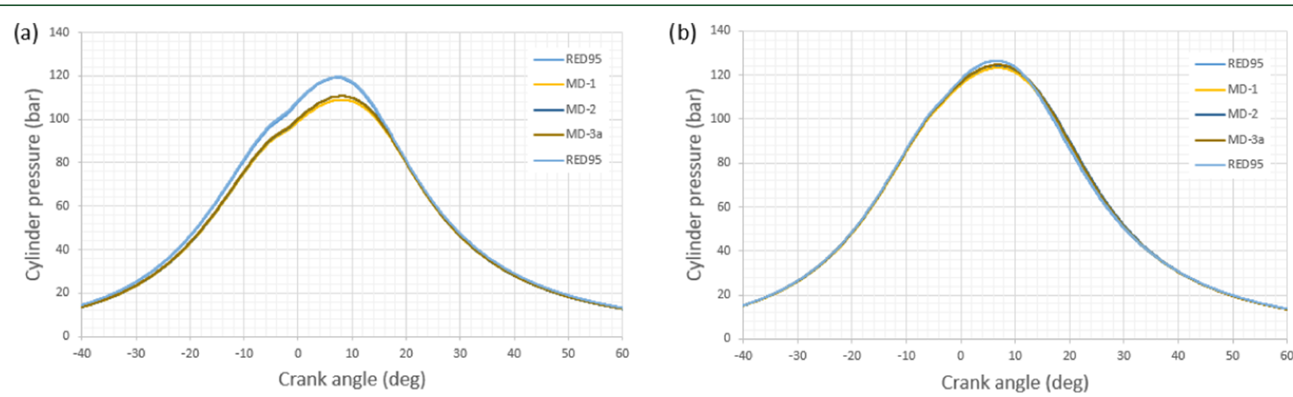

Figure 5. Cylinder pressures at load points (a) 50% at 1439 min^{-1} (438 Nm, 66 kW, B50) and (b) 50% at 1769 min^{-1} (384 Nm, 71 kW, C50).

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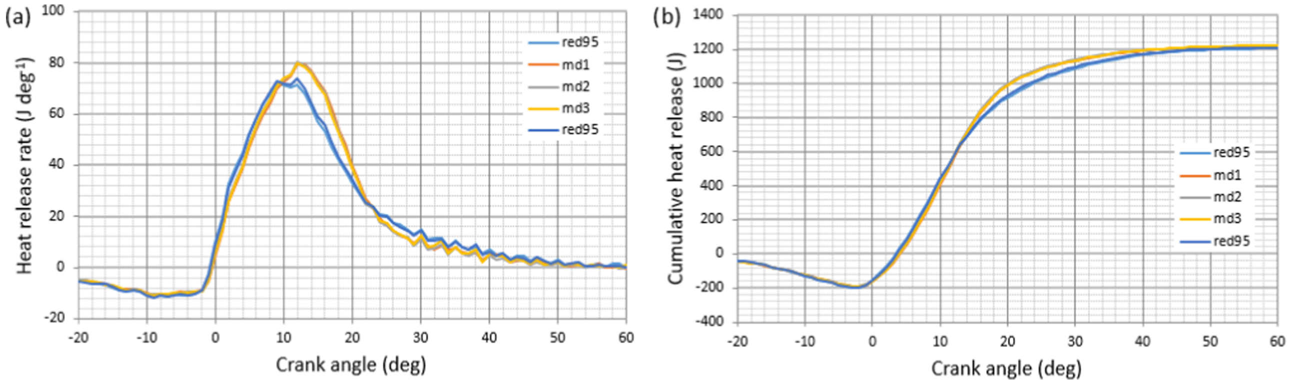

Figure 6. (a) Heat release rates and (b) cumulative heat releases. Engine load 50% at 1439 min^{-1} (438 Nm, 66 kW, B50).

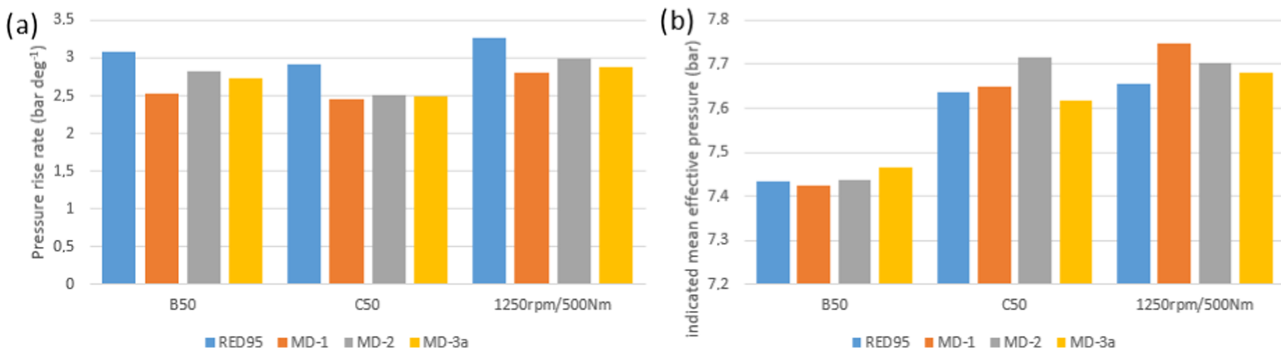

Figure 7. (a) Pressure rise rate and (b) indicative mean effective pressure. B50 = 1439 min^{-1}, 438 Nm, 66 kW; C50 = 1769 min^{-1}, 384 Nm, 71 kW.

ignition improver additive than the other fuels, to study whether manifold injection could enable using these fuels with particularly poor ignition properties. The cetane number of the MD-5 fuel was particularly low.

In Figure 8, the cylinder pressure traces show the effect of the intake manifold injection. The blue trace illustrates the

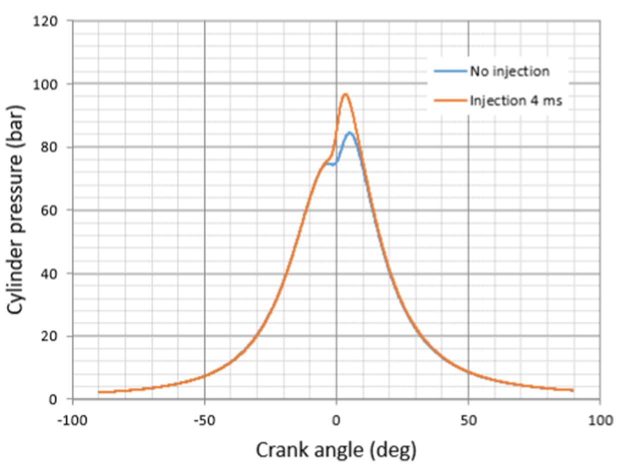

Figure 8. MD-5 fuel utilizing intake injection at a low load point (50 Nm at 900 min^{-1}).

cylinder pressure without manifold injection, and higher (orange trace) and more stable cylinder pressure was achieved when the intake manifold injection was utilized. No exhaust emission benefit was achieved with manifold injection in these tests (Figures S7 and S8, Supporting Information). Interestingly, the NO_2 concentrations increased when injecting ED95 into the intake manifold regardless of the main fuel type tested (ED95 or MD95). For example, NO_2 concentration increased from 9 to 40 ppm when manifold injection was applied, whereas NO_x concentrations were 124 and 130 ppm, respectively. In the fumigation concept, increased NO_2 concentrations were also observed by Cheung et al.[51] The manifold injection system could further be developed in both flow design and main injection functionality to investigate the potential of the concept.

4. CONCLUSIONS

Several MD95 methanol blends were clean-burning in the Scania EEV Ethanol DC9 270 hp when glycerol ethoxylate GE and poly(ethylene glycol) PEG type ignition improvers were used. Particularly low aldehyde emissions were observed for MD-2 containing GE ignition improver and RME ester, although gaseous emissions were also low for MD-3 fuel containing DNPE ether and for MD-1 and ED95 fuels combining PEG ignition improver and commercial lubricity additive.

Elevated particulate emissions (both mass and number) were observed for fuels containing RME as lubricity additive (MD-2 and MD-3) and to a lesser extent for MD-1 and ED95 fuels. Particles appeared to be semivolatile “liquid” material originating from the additives. Semivolatile material could be removed efficiently by the oxidation catalyst belonging to the commercial Scania alcohol engine concept. Cylinder pressure analysis showed similar performance for MD95 and ED95 fuels. For lower dosing of ignition improver additive in MD95 fuels, fuel injection into the intake manifold allowed running of the engine with stable cylinder pressure behavior. Overall, the results showed that the MD95 concept can be a potential solution for introducing environmentally friendly renewable methanol fuel for smaller vessels.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.9b02654.

Scania ethanol engine; emission test procedure; results on solubility, emissions, cylinder pressure analyses and manifold injection (PDF)

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Notes

The authors declare no competing financial interest.

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