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Exhaust emissions on a four-stroke engine from bio residual fuel containing tire pyrolysis oil and FAME

Fuels - Alternative & New Fuels

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ABSTRACT

The 7th revision of ISO 8217 was published in May 2024. The major evolution of this revision is the new bio-residual marine fuels table that considers the blending of FAME (compliant with EN 14214) at any ratio. The use of sustainable marine fuels (SMF) is one of the solutions to reduce the carbon footprint of the shipping, but the availability of FAME is not sufficient to satisfy all volume demand. TotalEnergies is looking for alternative sustainable bases not covered by EN 14214 which can be suitable for marine fuel blending. A dedicated evaluation protocol has been developed from the laboratory evaluation to the sea-trial. Tire pyrolysis oil (TPO), a bio-based compound derived from the recycling of used tires, has been identified as a relevant basis that can be used in marine residual fuel recipes, and which contributes to the reduction of the carbon footprint of the blend.

A blend formulated with TPO, FAME and fossil bases was validated at the lab scale and prepared in a sufficient quantity to be tested on marine bench at CReS (TotalEnergies Research Center), equipped with a four-stroke MAN diesel engine compliant with Tier II regulations. The performance of the bio-residual marine fuel was compared with the reference VLSFO obtained from the same fossil bases and a bio-VLSFO containing only FAME and the fossil bases.

Emissions of gaseous pollutants (CO, SO2, NOx,) and black carbon were measured according to current regulations on the standardized E2 cycle used by MAN for the approval of its engines. The results show that the VLSFO containing TPO and FAME blend does not cause any problems in use, has lower NOx emissions than MGO (reference fuel considered by IMO), and has black carbon emissions of the same order of magnitude as VLSFO and bio-VLSFO.

The results of the laboratory study and of the emissions measurements on the marine engine test are given in this document.

1 INTRODUCTION

The 7th revision of ISO 8217 was published in May 2024. One of the major evolutions of this revision is the allowance of the blending of FAME (Fatty Acid Methyl Ester) (compliant with EN 14214) in marine distillates and marine residual fuels without any limitation. The use of Sustainable Marine Fuels (SMF) is one of the straightforward solutions to reduce the carbon footprint of the shipping, and as already performed for bio-VLSFO (Very Low Sulfur Fuel Oil) containing FAME [1], it appears essential to characterize the emissions from the different Sustainable Marine Fuels which are currently being developed. This paper describes the combustion behavior and pollutants emissions of bio marine distillate at different blending ratio of bio components such as FAME and HVO (Hydrotreated Vegetable Oil) and the bio residual marine fuel containing FAME and TPO (Tire Pyrolysis Oil). These fuels were evaluated in TotalEnergies research center dedicated to fuels and lubricants activities. The testing facility is described in the following paragraph whereas the fuels characteristics are given in paragraph 3.

2 MARINE ENGINE TESTING FACILITY

2.1 Test bed description

The tests were performed on the marine test bench equipped with a four-stroke five-cylinders in-line medium speed marine Diesel engine (MAN 5L16/24), IMO Tier-I compliant. The engine, coupled with a 430kW alternator is described in Table 1.

Table 1. Test engine specification

Engine	MAN 5L16/24
Production year	2003
Cycle	4-stroke
Configuration	In-line
Bore	160mm
Stroke	240mm
Cylinders number	5
Emissions regulation	IMO Tier I
Rated speed	1000rpm
Rated power	450kW
Fuel acceptance	MGO, HFO, VLSFO, biofuels

The fuel supply system based on two main lines allows to operate the engine from high-capacity tanks of MGO (Marine Gas Oil) and VLSFO. For prototype fuels evaluations, a heated *Vortex* tank connected to a third fuel line is specifically used. The set-up allows to operate with blends based on distillate or residual fuels. This specific installation, used for this investigation, is described in following Figure 1.

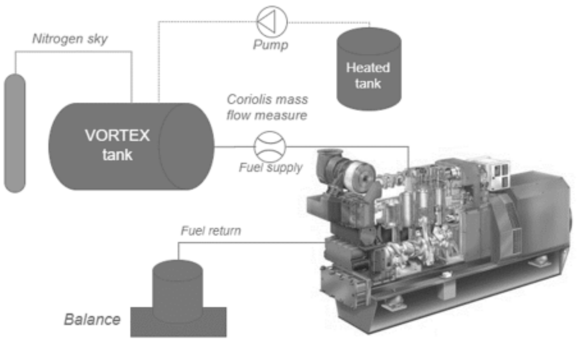

Figure 1 Prototype fuel supply system

A Coriolis mass flow meter is installed to measure intake fuel mass flow, whereas return fuel is collected in a tank and weighted thank to high precision balance. Effective consumed fuel is calculated by removing return flow from intake mass flow.

The stability of the engine operating conditions is controlled and monitored thank to an exhaustive instrumentation on intake air, exhaust gases, cooling and lubrication systems. Control actuators allowed to get repeatable conditions from a fuel to another, considering stability criteria described in Table 2.

Table 2. Engine operation stability conditions

Measurement	Maximum allowed deviation	Category
Coolant temperature	+/-2°C	Regulation Stability
Oil temperature	+/-2°C	
Engine speed	+/-3rpm or 1% of rated speed	
Air intake temperature	+/-1°C	
Intake air pressure	+/-2°C	Operating point / Stability
Exhaust gas temperature (mean value)	+/-5°C or 1%	
Torque / Power	+/- 2%	
Fuel consumption	+/-2% of engine max value	

2.2 Emissions measurement setup

For this test campaign *TotalEnergies Air Quality Laboratory (LQA)* prepared and performed emissions measurements in the exhaust line. Pollutants selected for measurement were combustion gases (CO, CO_2, NO_x, SO_2, total organic carbon TOC), N_2O and Black Carbon.

The exhaust gases sampling was located 10m downstream the turbine outlet, with straight pipes upstream and downstream the sampling, as shown in Figure 2. The sampling point then complies with the applicable standards (NF X 44-052 / NF EN 13284-1 / EN 15259).

Figure 2. Gas sampling in engine exhaust line

The HORIBA PG250, gas analyzer for compliance testing of NO_x, SO_2, CO, CO_2, and O_2, was used for continuous measurements. The HORIBA PG-250 uses NDIR (pneumatic) for CO and SO_2 measurements, NDIR (pyrosensor) for CO_2, Chemiluminescence (cross flow modulation) for NO_x and Galvanic Cell for O_2 measurements.

The hydrocarbon content in the exhaust gases was determined in accordance with the principles of NF EN 12619-1 using a JUM 109L analyzer (continuous flame ionization detector). A sample of the gaseous effluent is continuously pumped in the duct. Organic compounds are detected by passing the filtered flue gas through an ionizing flame. This stream of ionized compounds, proportional to the TOC content, is then measured and results are expressed in mg/Nm^3 methane equivalent.

The Horiba VA3000 uses the principle of infrared correlation (NDIR) to measure nitrous oxide (N_2O) in a continuous sampling. It is equipped with an optical CO_2 filter to overcome interference caused by this gas.

Calibration and checks of the different analyzers were performed using certified commercial standard gas cylinders.

Water vapor was measured during sampling using a condensation / adsorption technique to provide emissions results expressed in dry gas concentration.

Black carbon emissions of the different fuels were measured using a photoacoustic analyzer (AVL Microsoot sensor 483). Photo-acoustic techniques are direct, in situ measurements of the aerosol absorption coefficient at the wavelengths of the light source(s) employed. They quantify the fraction of absorbed optical energy that is rapidly transferred into the surrounding air. Light, generally in the form of a laser beam, is incident on a particle suspended in air; some of the light is transmitted, some scattered, and if the particle has a non-zero imaginary component of the refractive index, some is absorbed and heats the particle. For small particles, the heat is rapidly transferred to the surrounding air, and if the incident light is power modulated, an outgoing acoustic wave at the modulation frequency is generated. Generally, an acoustic resonator is employed to enhance the acoustic signal and to exclude and reduce acoustic noise. The resulting acoustic pressure is quantified with a microphone where the resulting signal is proportional to the aerosol absorption coefficient.

All emissions measurement equipment were metrologically controlled and certified compliant before the tests.

Exhaust flow rate was determined following ISO 10-780 scanning the velocity field with a pitot tube was used for pollutants mass flow calculation.

In parallel of the set-up of LQA a FTIR (InfraRed spectroscopy) measurement device IAG Versa 06 was installed to be evaluated by comparing the results with the normalized installation

2.3 Test protocol

This test is based on NO_x homologation test from MARPOL with some adaptations. Each fuel is tested through a 5,5 hours sequence, shown in Figure 3. This sequence was performed twice for each fuel to confirm emissions measurements and thus get robust evaluation of the fuels.

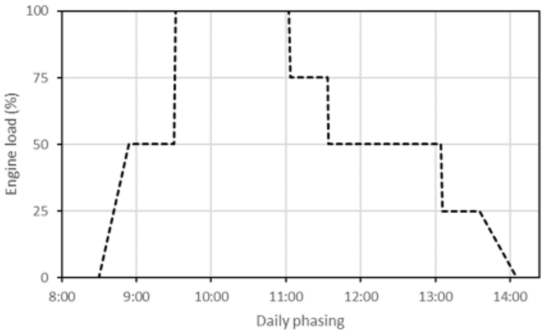

Figure 3. Daily test sequence

Engine warm-up is performed at 50% and then 100% load. After thermal stabilization, engine is operated at 4 different load stages (100 – 75 – 50 – 25% load). On each operating condition, emissions measurement starts after stability checks. 100% load and 50% load operations are longer, to get sufficient running time to perform additional particle samplings.

Reference tests with MGO were performed regularly during the campaign (cf. Figure 4) to assess test repeatability and to check any potential drift of engine operation or emissions measurement.

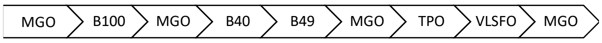

Figure 4. Fuel testing sequence

The whole test protocol, including testing equipment, emissions measurements setup and test plan, was shared with and certified by *Bureau Veritas* in a previous test campaign.

3 FUEL BLENDS INVESTIGATED

Two different test campaigns were performed. One dedicated to bio-distillate marine fuels and the other one to bio-residual marine fuel.

3.1 Bio-distillate marine fuel blends

Bio-distillate marine fuel blends were prepared using a marine gasoil (MGO), the heavy fraction of an Hydrotreated Vegetable Oil (HVO) and a Fatty Acid Methyl Ester (FAME) compliant with EN 14214 specifications.

The main characteristics of the bases are summarized in Table 3.

Table 3. Main characteristics of the bases used for bio-distillate fuel blend

Component			HVO	MGO	FAME
Characteristic	Unit	Reference Test method	Analysis		
Viscosity@40°C	mm²/s	ISO 3104	3.252	2.321	4.418
Density@15°C	kg/m³	ISO 12185	783.2	840.6	883.0
Pour point	°C	ISO 3016	-60	-9	-12
Flash point	°C	ISO 2719	133	66,0	141,5
Acid Number	mgKOH/g	ASTM D664	< 0.05	-	0.37
ECN	-	IP 541	> 70	53.9	62.2

The recipes of the bio-distillate marine fuel blends are given in Table 4 including the main characteristics measured on the blends.

Figure 5 shows the formulation diagram based on the quality of the bases as described in Table 3 and the application of the blending laws when appropriate. The formulation diagram does not emphasize any constraining characteristic which is obvious as all three components already meet the DMA / DFA specifications.

The different blends tested are represented on the diagram by the black symbols. The composition in the diagram is expressed in volume percentage whereas the recipes are given in mass percentage in Table 4.

Table 4. Recipes and main characteristics of the bio-distillate marine fuel blends

DFA grade			B40	B49	B100
Component			Composition of the blends (mass %)		
MGO			60	51	
FAME			40	40	7
HVO				9	93
Characteristic	Unit	Reference Test method	Analysis		
Viscosity@40°C	mm²/s	ISO 3104	3.586	3.619	3.288
Density@15°C	kg/m³	ISO 12185	853.1	850.6	789.3
Pour point	°C	ISO 3016	-9	-9	-6
Cloud point	°C	ISO 3015	-1	-3	-6
CFPP	°C	IP 309	-4	-8	-8
Oxidation stability	h	EN 15751	27.6	28.3	89.1
	min	EN 16091	65.60	66.46	162.2
Lubricity	µm	ISO 12156-1	171	165	177
ECN	-	IP 541	56.9	59.7	72.0

These 3 DFA blends meet the DFA specifications as given in ISO 8217:2024.

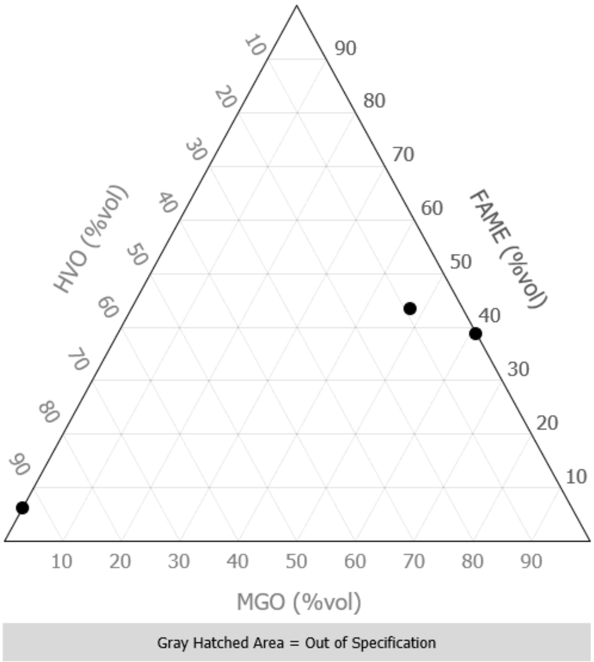

Figure 5. Formulation domain for bio-distillate fuel blend

3.2 Bio-residual marine fuel blend

The bio-residual marine fuel blend was produced from petroleum bases (heavy residue and fluxant) samples in a refinery, commercial FAME produced by Saipol (compliant with EN 14214 specifications) and Tire Pyrolysis Oil (TPO) supplied by TotalEnergies Trading & Shipping Department.

The main characteristics of the bases are summarized in Table 5.

Table 5. Main characteristics of the bases used for bio-residual marine fuel blend

Component			Heavy residue	Fluxant	FAME	TPO
Characteristic	Unit	Reference Test method	Analysis			
Viscosity@50°C	mm²/s	ISO 3104	2710	2.715	3.626	5.136
Density@15°C	kg/m^3	ISO 12185	965.5	840.6	883.0	948.7
CCAI	-		809	796	828	883
VGC	-	ASTM D2501	0.86	0.83	0.86	0.93
Sulfur content	mg/kg	ASTM D2622	6560	10	0	9340
Carbon Residue	%	ISO 10370	11.26	-	-	1.62
Pour point	°C	ISO 3016	18	-9	-12	-18
Flash point	°C	ISO 2719	> 120	66,0	141,5	59,5
Acid Number	mgKOH/g	ASTM D664	-	-	0.37	8.58
ECN	-	IP 541	28.9	53.9	62.2	6.6

The formulation diagram has been determined using our predictive tool based on the characteristics of the components and the blending laws when appropriate.

The constraining characteristics are the sulfur content and the minimum / maximum viscosity of the targeted grade (from 20mm²/s to 80mm²/s for RF 80 and minimum 80mm²/s for RF 180).

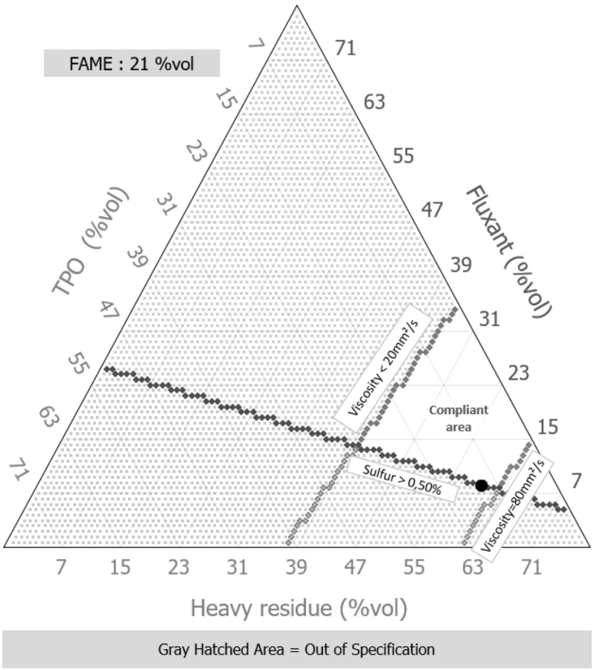

Figure 6. Formulation domain for bio-residual marine fuel

The objective of the recipe was to saturate the sulfur content with a total amount of non-petroleum compounds around 30% mass.

The composition of the bio-VLSFO and the main characteristics of the blend are given in Table 5 and compared to RF 80 specification limits.

Table 5. Composition and main characteristics of bio-VLSFO

DFA grade			RF 80	
Component			mass %	
Heavy residue			65	
Fluxant			8	
FAME			20	
TPO			10	
Characteristic	Unit	Reference Test method	Analyses	RF80 spec
Viscosity@50°C	mm²/s	ISO 3104	55,69	> 20 < 80
Density@15°C	kg/m^3	ISO 12185	934,9	< 991
CCAI	-	-	820	< 870
Sulfur content	%		0,474	< 0,50
Flash point	°C	ISO 2719	89,0	> 60
Acid Number	mgKOH/g	ASTM D664	1,31	< 2,5
Pour point	°C	ISO 3016	0	< 30
Potential total sediment (TSP)	%	ISO 10307-2A	0,01	< 0,10
Net heat of combustion	Mj/kg	ASTM D 240	40,715	Report
Estimated Cetane Number (ECN)	-	IP 541	36,4	-

The RF 80 blend meets all specifications as indicated in ISO 8217:2024 Table 3 including clauses 5 to 10.

4 RESULTS

The main focus is to assess the impact of the sustainable marine fuel blends on exhaust gas emissions of interest: NOx, and Black Carbon.

Regarding NOx emissions, correction of humidity and temperature were applied as described in the NO$_x$ Technical Code, chapter 5.12.4.6.

All gas emissions concentrations were then converted to Specific Emissions based on exhaust gas velocity measurement and engine output power measurement.

To aggregate the different measurement on the engine running points, we are using the ponderation method, used in the E2 cycle and defined in the NO$_x$ Technical Code, chapter 3.2.3, which combines Equation 1 in association with weighting factors, shown in Table 6.

$$NOx = \frac{\sum \alpha_i \times Power_i \times SE_{NOx_i}}{\sum \alpha_i \times Power_i} \quad (1)$$

Where $\propto_i$ is the weighting factor, $Power_i$ is the engine power of the operating point and SE_{NOx_i} is the NOx concentration measured at the exhaust pipe.

Table 6. E2 test cycle weighting factors

Test cycle type E2		
Speed	**Power**	**Weight factor**
100%	100%	0.2
100%	75%	0.5
100%	50%	0.15
100%	25%	0.15

4.1 Bio-distillate marine fuel blends

On Figure 7 we can observe different behavior due to the composition of the blends. Regarding the B100 (7% FAME / 93% HVO), the modification of the compromise between NOx, particles and fuel consumption with the physic and chemical characteristics of HVO could lead to the decrease of the NOx emissions [2]. Mizushima et al. [3] observed also that the higher H/C ratio of the HVO has a positive influence on the NOx emissions.

With blend of FAME (B40: 60% MGO / 40% FAME and B49: 51% MGO / 40% FAME / 9% HVO) we can notice an increase of NOx emissions due to oxygen content which can be partially offset with the incorporation of HVO. However, we are into the 10% allowance of the NOx technical code. This type of fuel blends can be also used on board a ship. This behavior correlates with measurements done on board with B50 (50% of FAME/50% MGO).

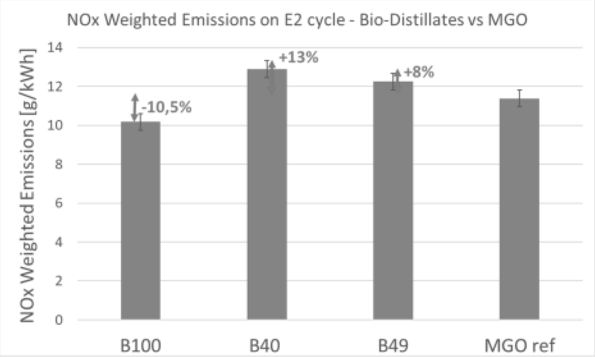

Figure 7. NOx weighted emissions of MGO and bio-distillate marine fuels

Regarding Black Carbon emissions, with all the bio-distillate marine fuels we can observe on Figure 8 a decrease either due the aromatic-free composition of HVO and FAME or the oxygen content of FAME that allows to boost the oxidation of the particles during the combustion.

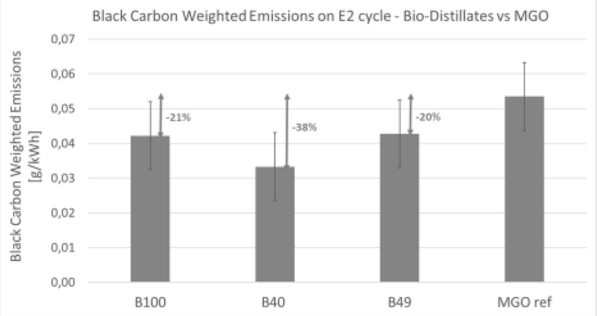

Figure 8. Black Carbon weighted emissions of MGO and bio-distillate marine fuels

In addition to NOx and Black Carbon emissions, it is also interesting to study the CO2 emissions. As observed in Figure 9, we can see a significant reduction of CO2 emissions with B100 which is mainly HVO. This can be explained by the higher H/C ratio, the higher lower heating value in mass, which improve power density compared to diesel fuel and the higher thermal efficiency achieved with a paraffinic fuel [2].

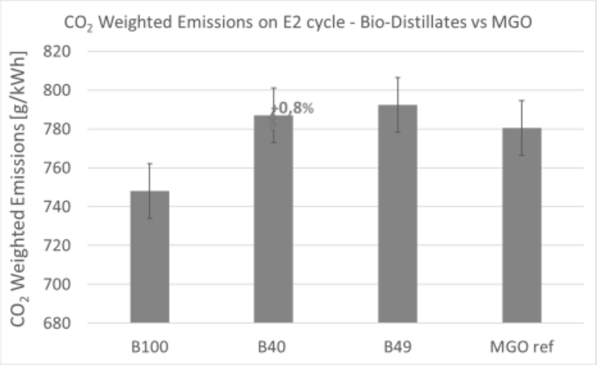

Figure 9. CO_2 weighted emissions of MGO and bio-distillate marine fuels

4.2 Bio-residual marine fuel blend

On one hand, the NOx weighted emissions of VLSFO and bio-VLSFO B30 containing 30% of FAME are of the same order of magnitude and significantly lower than NOx emissions from marine distillate (MGO). On the other hand, the NOx weighted emissions of the VLSFO containing FAME and TPO are also lower than the NOx weighted emissions of VLSFO and B30 blend with FAME only. This could be a consequence of the aromatic nature of TPO that deteriorates the combustion quality compared to VLSFO and B30 which has a straightforward impact on NOx emissions which are decreased. The counterpart is usually an increase of Black Carbon emissions but, as shown on figure 11, they are eventually in the same order of magnitude as VLSFO but obviously higher than MGO. The increase of the Black Carbon emissions for VLSFO containing FAME and TPO is not significant.

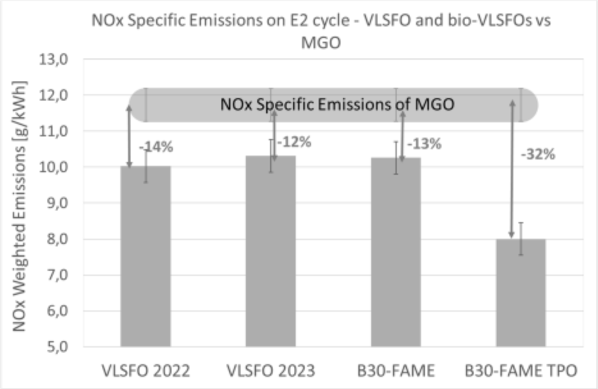

Figure 10. NOx weighted emissions of VLSFO and Bio-VLSFO

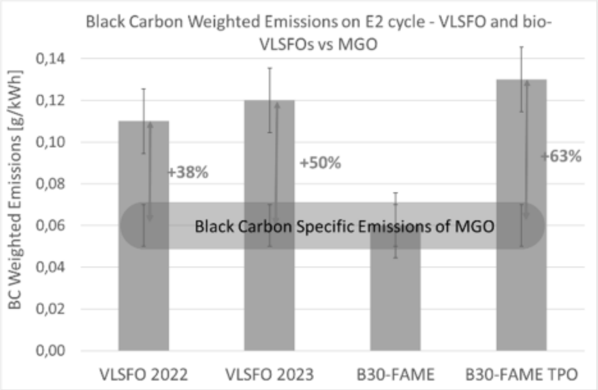

Figure 11. Black Carbon weighted emissions of VLSFO and bio-VLSFO

5 CONCLUSIONS

Those tests performed on a four-stroke marine engine bench allow the comparison of pollutants emissions from different fuels with MGO which is the reference fuel. The pollutants emissions were measured on the E2 test cycle as described in the NO$_x$ technical code.

The NOx emissions from bio-distillate marine fuels are within the tolerance of the NOx technical code compared to the NOx emissions from the reference fuel whereas the Black Carbon emissions are significantly lower compared to MGO.

The better ignition and combustion quality of MGO (higher ECN – Estimated Cetane Number) compared to VLSFO and bio-VLSFO leads to higher temperature in the combustion chamber and therefore higher NO$_x$ emissions. In addition, NO$_x$ emissions from bio-VLSFO are of the same order of magnitude or sensitively lower than NO$_x$ emissions from VLSFO. The NOx emissions from bio-VLSFO containing TPO are even lower than the NOx emissions from VLSFO and bio-VLSFO.

Black Carbon emissions from bio-VLSFO containing TPO are in the same order of magnitude compared to standard VLSFO and obviously higher than Black Carbon emissions from MGO.

6 DEFINITIONS, ACRONYMS, ABBREVIATIONS

BC: Black Carbon

CCAI: Calculated Carbon Aromaticity Index

ECN: Estimated Cetane Number

DFA: Distillate Marine Fuel with FAME content

DMA: Distillate Marine Fuel

FAME: Fatty Acid Methyl Ester

FTIR: Fourier Transformation Infra-Red

HVO: Hydrotreated Vegetable Oil

LCV: Low Calorific Value

LQA: Laboratoire de Qualité de l’Air

MGO: Marine Gas Oil

NDIR: Non-Dispersive Infra-Red

NO$_x$: Nitrogen Oxides

TPO: Tire Pyrolysis Oil

VLSFO: Very Low Sulfur Fuel Oil

7 ACKNOWLEDGMENTS

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9 CONTACT

This is where the main author information is given, if desired, such as background, education, e-mail address, and web address. This is an optional section.