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Operation of Marine Diesel Engines on Biogenic Fuels: Modification of Emissions and Resulting Climate Effects

Andreas Petzold,*[†] Peter Lauer,[‡] Uwe Fritsche,[§] Jan Hasselbach,[†] Michael Lichtenstern,[†] Hans Schlager,[†] and Fritz Fleischer[‡]

[†]Deutsches Zentrum für Luft- und Raumfahrt, Institut für Physik der Atmosphäre, 82234 Oberpfaffenhofen, Germany

[‡]MAN Diesel & Turbo SE, Stadtbachstrasse 1, 86135 Augsburg, Germany

[§]Öko-Institut — Institute for Applied Ecology, Energy & Climate Division, Rheinstrasse 95, 64295 Darmstadt, Germany

S *Supporting Information*

ABSTRACT: The modification of emissions of climate-sensitive exhaust compounds such as CO_2, NO_x, hydrocarbons, and particulate matter from medium-speed marine diesel engines was studied for a set of fossil and biogenic fuels. Applied fossil fuels were the reference heavy fuel oil (HFO) and the low-sulfur marine gas oil (MGO); biogenic fuels were palm oil, soybean oil, sunflower oil, and animal fat. Greenhouse gas (GHG) emissions related to the production of biogenic fuels were treated by means of a fuel life cycle analysis which included land use changes associated with the growth of energy plants. Emissions of CO_2 and NO_x per kWh were found to be similar for fossil fuels and biogenic fuels. PM mass emission was reduced to 10−15% of HFO emissions for all low-sulfur fuels including MGO as a fossil fuel. Black carbon emissions were reduced significantly to 13−30% of HFO. Changes in emissions were predominantly related to particulate sulfate, while differences between low-sulfur fossil fuels and low-sulfur biogenic fuels were of minor significance. GHG emissions from the biogenic fuel life cycle (FLC) depend crucially on energy plant production conditions and have the potential of shifting the overall GHG budget from positive to negative compared to fossil fuels.
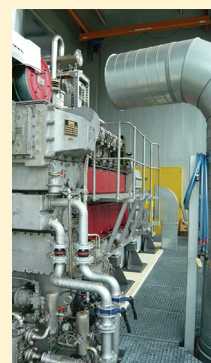
1. INTRODUCTION

The use of biogenic fuels for stationary power generation or for propulsion in shipping gains increasing importance in the framework of CO_2 reductions and the use of energy from renewable sources. Since biomass or vegetable oils which are used for biogenic fuel production do contain only trace amounts of sulfur, the resulting fuel is characterized by very low fuel sulfur content (FSC). While burning high-sulfur fuels in shipping generates particulate matter (PM) emissions dominated by sulfates,[1−6] the use of low-sulfur fossil fuel reduces the emission of PM significantly.[7] A similar effect is expected for low-sulfur biogenic fuels, which however have not been studied yet. This change in emission properties contributes to reducing health impacts from shipping emissions[8,9] as well as to reducing particulate matter-related short-lived climate forcers emitted by marine diesel engines.[5,10−12] Exploring the potential benefits of biogenic fuel use in shipping or for stationary power generation is therefore important for several reasons.

The knowledge on emission characteristics and on resulting climate impacts of marine diesel engines operating on different biogenic fuels is very limited. In the framework of the German *klimazwei* program, the project BIOCLEAN focused on the emissions from a marine diesel engine using fossil and biogenic fuels. The simultaneous consideration of climate-sensitive trace species like NO_x, PM, black carbon (BC), and sulfur-containing particle precursors and of the most important greenhouse gas CO_2 allowed for the investigation of trade-off effects of CO_2

emissions reduction and potentially increasing emissions of other climate-active trace constituents. GHG emissions associated with the production of biogenic fuels[13,14] were included by means of a fuel life cycle analysis which considered land use changes (LUC) associated with the growth of energy plants for fuel production.[15−17] Several studies identified LUC-related GHG emissions as a key factor of the overall GHG emission balance of biogenic fuels.[18−20]

2. EXPERIMENTAL SECTION

2.1. Overall Approach. We investigated the emissions of CO_2, NO_x, hydrocarbon compounds (HC), SO_2, and PM in terms of particle number, particle size, sulfate, black carbon (BC), and organic matter (OM) for different fuels. The set of fuels included HFO with a FSC of 2.17 weight-% (wt-%) as the fossil high-sulfur reference fuel, MGO with an FSC of <0.1 wt-% as a fossil low-sulfur fuel, and palm oil, soybean oil, sunflower oil, and animal fat from food production as fuels from biogenic sources. These degummed and deacidified but not transesterified first generation biogenic fuels can be used directly in marine diesel engines which are designed to operate on residual fuels with its injection system being optimized for handling highly viscous

Table 1. Fuels Used in BIOCLEAN Including Fuel Specific CO_2 Emissions

fuel	properties	specific CO_2 emission
palm oil	large availability on the global market, very good fuel properties, critical production conditions	2.83 kg CO_2/kg fuel 0.651 kg CO_2/kWh
soybean oil	potential technical problems from unsaturated fatty acids, energy plant production competes with food plant production	2.86 kg CO_2/kg fuel 0.660 kg CO_2/kWh
sunflower oil	biogenic fuel from regional markets, only of regional interest	2.87 kg CO_2/kg fuel 0.655 kg CO_2/kWh
animal fat	waste products from food production, only of regional interest	2.82 kg CO_2/kg fuel 0.651 kg CO_2/kWh
heavy fuel oil (HFO)	conventional reference fossil fuel	3.19 kg CO_2/kg fuel 0.660 kg CO_2/kWh
marine gas oil (MGO)	low-sulfur fossil fuel	3.195 kg CO_2/kg fuel 0.639 kg CO_2/kWh

Table 2. Fuel Chemical Composition and Properties

fuel	HFO	MGO	palm oil	animal fat	soybean oil	sunflower oil
category	residual	distillate	biogenic	biogenic	biogenic	biogenic
type	RM grade	DMA grade	vegetable	animal	vegetable	vegetable
viscosity [mm^2/s]	719 @ 50 °C	2.6 @ 40 °C	29 @ 50 °C	31 @ 50 °C	23 @ 50 °C	23 @ 50 °C
density @ 15 °C [kg/m^3]	982	838	916	914	923	924
hydrogen [weight-%]	10.45	12.72	11.00	11.20	11.20	11.00
carbon [weight-%]	86.94	87.08	77.30	77.00	78.10	78.30
sulfur [weight-%]	2.17	<0.1	7.2 ppm	2.8 ppm	<0.1	1.4 ppm
nitrogen [weight-%]	0.42	<0.1	-	-	-	-
oxygen [weight-%]	-	-	11.50	11.60	10.50	10.50
ash [weight-%]	0.017	0.0011	0.0016	0.0017	<0.001	<0.001
calorific value [MJ/kg]	40.435	42.966	37.144	37.292	37.264	37.268

fuels. They cannot, however, be used in e.g. automotive diesel engines.

Table 1 summarizes the fuels including specific CO_2 emissions with respect to generated power in kWh and consumed fuel mass in kg. Properties and chemical composition of the fuels including FSC are compiled in Table 2. The main differences between fossil and biogenic fuels are related to the energy content per mass which is significantly higher for fossil fuels (HFO: 40.4 MJ kg^{-1}; MGO: 43.0 MJ kg^{-1}) than for biogenic fuels (average: 37.3 MJ kg^{-1}) and to the resulting specific CO_2 emissions per kg of burned fuel.

One single-cylinder test engine with 400 kW power running on 750 rpm served as emission source. The externally charged engine of type 1L32/44 is characterized by a stroke of 440 mm, a bore of 320 mm, and a compression ratio of 16.2. The measurement of exhaust gas constituents was positioned downstream the exhaust gas receiver to compensate for pressure pulsation and pressure relief and before the exhaust gas exit to atmosphere. The measurement of exhaust gas components NO_x, HC, CO, CO_2, and O_2 was conducted according to ISO-8178 by chemilumines-cence, flame ionization, nondispersive-infrared, and paramagnetic detection, respectively. PM mass emission measurement was performed with a partial flow dilution system according to ISO-8178.

For each fuel, an engine load sequence of 100%, 75%, 25%, 10%, and again 100% was investigated. Each run lasted for approx 1 h; the whole test sequence per fuel required one full day of operation. The test was completed by a 100%-load continuous

run which lasted for 100 h in order to investigate potential corrosive effects of the fuels.

2.2. Instrumentation. For our studies, a setup almost similar to the one from previous marine diesel engine emissions studies[5] was applied. The instrumentation used for the measurement of aerosol microphysical properties consisted of Condensation Particle Counters (CPC, TSI Models 3010/3760A, uncertainty <5%) with lower cutoff diameters of 0.01 μm, 0.03 μm, and 0.08 μm, one Differential Mobility Analyzer (DMA, TSI Model 3071) covering particle diameters (d_p) from 5 to 200 nm, one Optical Particle Counter (OPC, GRIMM Model 1.129) for the size range d_p > 250 nm, and one Multi-Angle Absorption Photometer (MAAP, Thermo Instruments Model 5012) for BC mass concentration measurement (BC measurement uncertainty 12%, conversion factor 6.6 m^2/g at a wavelength of 630 nm). Volatile and nonvolatile aerosol compounds were separated by a thermodenuder operating at 250 °C. Accuracy and reproducibility of the online instruments are reported in a recent method evaluation study for emission measurement techniques.[21] Since for marine diesel engines no reference method for PM measurement has been developed yet, PM measurement methods developed for gas turbines have been applied.

The exhaust gas samples for online aerosol microphysics measurements were diluted by a factor of 1000 for DMA, OPC, and MAAP and by an additional factor of 100 for CPC, using multiple isokinetic dilution stages (Palas Model VKL-10). Details on the setup are given in the Supporting Information (SI), see Figure SI1.

Table 3. Emission Factors per kWh of Generated Power[a]

	CO₂, kg	NOₓ, g	SOₓ, g	CO, g	HC, g	CH₂O, g	PM_dry, mg	SO₄, mg	OM, mg	EC, mg	Ash, mg	BC, mg	N_total 10¹⁴	N_nv 10¹⁴	f_PF[§]
HFO															
100%	0.675	14.12	9.13	0.20	0.072	0.013	776	613	104	21	38	4.8	3.50	2.41	4.72
75%	0.679	15.33	9.17	0.19	0.083	0.007	756	581	129	13	33	10.1	14.50	3.66	4.70
25%	0.898	17.45	11.67	0.70	0.095	0.008	423	236	128	15	44	22.9	24.47	6.30	3.55
10%	1.69	26.09	23.3	2.37	0.29	0.026	1009	447	375	94	93	126.0	47.56	12.00	1.89
MGO															
100%	0.632	12.81	<0.40	0.17	0.170	N/A	89	9	70	8	2	0.9	N/A	N/A	5.05
75%	0.639	14.65	<0.40	0.17	0.300	N/A	72	5	58	7	2	1.3	N/A	N/A	5.00
25%	0.856	17.3	<0.54	0.64	0.660	N/A	87	4	68	12	3	4.3	N/A	N/A	3.73
10%	1.552	23.39	<0.97	2.67	2.030	N/A	301	8	226	62	5	32.5	N/A	N/A	2.06
PO															
100%	0.651	12.95	0.003	0.19	0.047	0.019	121	2	106	10	3	1.2	1.92	0.63	4.35
75%	0.652	14.38	0.003	0.15	0.037	0.011	191	2	178	8	3	1.6	46.44	1.93	4.35
25%	0.864	18.68	0.004	0.45	0.090	0.018	216	3	195	14	4	5.9	25.53	2.33	3.28
10%	1.563	25.7	0.008	1.57	0.340	0.050	794	4	716	65	9	33.0	53.88	4.67	1.81
AF															
100%	0.651	12.71	0.001	0.12	0.050	0.015	90	1	78	8	3	1.1	1.95	1.34	4.34
75%	0.651	14.29	0.001	0.10	0.030	0.008	169	1	157	8	3	1.9	54.27	2.25	4.33
25%	0.846	16.91	0.002	0.38	0.065	0.012	130	1	114	10	5	4.8	19.45	2.16	3.34
10%	1.503	23.71	0.003	1.37	0.265	0.034	352	5	302	34	11	25.5	69.58	5.18	1.88
SBO															
100%	0.659	14.03	<0.46	0.14	0.045	0.015	142	4	118	18	2	1.9	5.43	2.04	4.34
75%	0.662	15.33	<0.46	0.14	0.030	0.010	126	2	107	15	2	3.3	28.23	2.28	4.32
25%	0.864	18.63	<0.60	0.43	0.060	0.000	188	3	160	22	3	6.8	25.59	2.08	3.31
10%	1.563	27.11	<1.09	1.50	0.260	0.000	677	4	581	87	5	45.7	60.26	8.93	1.83
SFO															
100%	0.655	14.21	0.0006	0.14	0.043	0.014	145	2	117	24	2	1.7	2.10	0.71	4.38
75%	0.669	16.03	0.0007	0.14	0.040	0.013	188	5	162	19	2	1.8	33.81	1.04	4.29
25%	0.864	19.18	0.0008	0.42	0.080	0.013	211	1	185	22	3	5.2	24.75	1.27	3.32
10%	1.523	27.35	0.0015	1.50	0.330	0.046	919	4	833	77	5	23.9	65.59	3.02	1.88

[a] f_{PF} is the conversion factor from emission per kWh to emission per kg of fuel; listed fuels are heavy fuel oil (HFO), marine gas oil (MGO), palm oil (PO), animal fat (AF), soybean oil (SBO), and sunflower oil (SFO).

Filter stack samples were taken using an AVL 472 Smart Sampler modular dilution system (AVL, Graz Austria). Teflon filters (PALL T60A20) were analyzed gravimetrically for total mass according to ISO-8178. Preconditioned quartz fiber filters (Pallflex 2500 QAO) were analyzed for carbon species by multistep combustion and for sulfate by ion chromatography (5% measurement uncertainty). Multistep combustion analyzes organic carbon (OC) by sequentially heating the sample under helium to 620 °C. Subsequently, elemental carbon (EC) is analyzed by switching to oxygen and heating the sample to 700 °C (EC, OC measurement uncertainty 20%). Organic matter is calculated from OC by $OM \cong 1.20 \times OC$.[5,22] Detailed method descriptions and references for measurement uncertainties associated with the filter-based methods are given in ref 5.

Gas phase compounds were measured by IR absorption (CO₂), chemiluminescence (NOₓ), flame ionization detector (total HC), and Hantzsch method (CH₂O).[23] SO₂ was calculated from the fuel consumption and from the FSC. Fuel flow was measured by a Coriolis principle detector (Endress+Hauser Promass 63) located in the fuel supply and return line. The power output of the engine was measured by a calibrated AVL Zöllner water brake. Generally, all measurements and accuracy analyses were performed according to ISO-8178. Power-rated emissions with respect to kWh were converted into emissions per kg of used fuel based on the measured fuel flow.

3. FUEL LIFE CYCLE ANALYSIS

The general idea of CO₂-neutral biogenic fuels relies on the assumption that the CO₂ released during the combustion of biogenic fuels was previously extracted from the atmosphere during the growth of the energy plants. However, the production of biogenic fuels generates emissions of non-CO₂ greenhouse gases (CH₄, N₂O)[13] by crop growing, fertilization, and processing and of CO₂ from fossil fuel use during fuel production, fertilizer production, and transport.[14] Assessing the GHG budget of biogenic fuels requires not only the consideration of the conventional fuel life cycle but also the additional GHG emissions caused by a modification of land use (LUC = land use change).[15,18−20] Including all relevant sources of GHG emissions during biogenic fuel production and use is an indispensable prerequisite for an integrated assessment of climate impacts of biogenic fuels.

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In our study, the model GEMIS (Global Emissions Model for Integrated Systems; http://www.gemis.de) of Öko-Institut was applied.[24−27] The key data to describe the fossil (reference) and biogenic life cycle were taken from earlier work[24,25,27] and updated with regard to data for marine fuels, and the possible future use of tar-sand based synthetic crude oil (syncrude) as an alternative feedstock for fossil-based HFO and diesel. We used the global warming potential from ref 28 and assumed a time horizon of 100 years for integration.

For biogenic fuels, GEMIS not only calculates the life cycles but also explicitly includes LUC-related GHG emissions of biomass cultivation systems. For this, emissions from both direct and indirect LUC are modeled using IPCC-based factors for GHG emissions resulting from direct LUC and the so-called "iLUC factor"[29] to represent potential emissions from indirect effects associated with displacement of previous land use.[18] As biogenic fuels represent a broad variety of options stemming from a multitude of bioenergy cultivation and conversion systems as well as from many different countries, the application of GEMIS selected a subset of life cycles relevant for BIOCLEAN fuels. For imported biofuels (soybean and palm oil), the future development of both the cultivation systems (yield increases, use of mulch to reduce N fertilizer) and feedstock processing (oil mill, especially auxiliary electricity needs and wastewater treatment) as well as international transports of the bioenergy carriers were taken into account in the life cycle modeling. The domestic production and processing of first generation liquid bioenergy carriers is already in a mature state and offers little options for improvement so that no major change in GHG emissions are foreseen.[26,27]

With regard to the reference fossil fuel energy carriers, the life cycles include future changes in production (lower flaring and venting rates, higher offshore shares) and processing (improved refining) as well as changes in the import structure representative for Europe.[24] With the expected medium-term depletion of conventional resources ("peak oil"), unconventional production options such as crude oil from tar sands and shales will become more relevant so that syncrude-based HFO and diesel was added to the analysis as a potential longer-term marginal fuel.

4. RESULTS

4.1. Bulk Emission Properties. The set of investigated biogenic fuels demonstrated good combustion properties and did not cause significant increase in engine degradation and corrosion. The full set of measured emission factors is compiled in Table 3. For an engine load of 75% which is considered representative for cruising ship or for stationary power generation operation, the emissions relative to HFO per kWh of generated power are shown in Figure 1. Respective graphs for the other investigated engine loads are given in the SI.

Emissions of core gaseous species CO_2, CO, and NO_x do not vary significantly between fossil high-sulfur fuel HFO and low-sulfur fossil and biogenic fuels. A similar result is reported in ref 7 for a comparison of HFO and MGO. Emissions of gaseous hydrocarbon compounds relative to HFO are significantly increased for MGO by a factor of 2.4 (100% load) to 7.0 (10% load), while respective emissions for biogenic fuels are similar to HFO (10% load) or reduced at most to 40% (75% load). This increase in HC emissions for MGO may be linked to the measurement method, because for MGO exhaust the FID sensor detects all HC in the gas phase while for HFO, some of the hydrocarbons
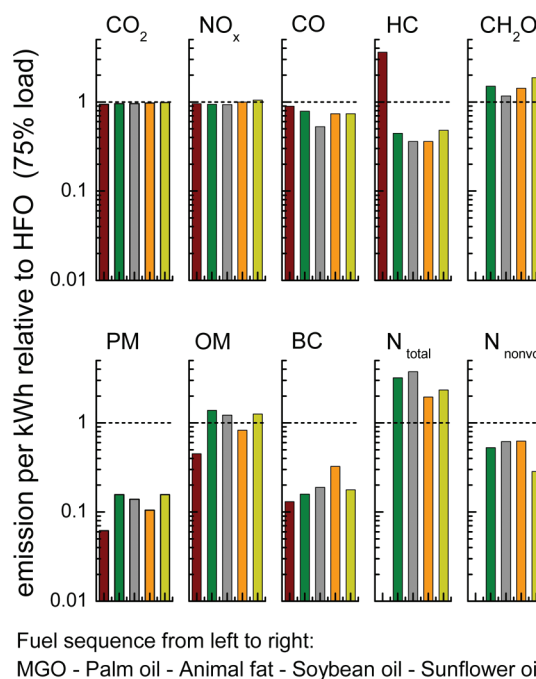

Figure 1. Emissions of gaseous (top row) and particulate (bottom row) compounds per kWh of generated power relative to heavy fuel oil (HFO) as the fossil sulfur-rich reference fuel for investigated fuels marine gas oil (MGO) and biogenic fuels at 75% engine load; used abbreviations for particulate matter compounds are explained in the text.

appear in the condensed phase. Formaldehyde (CH_2O) emissions are slightly enhanced by 26−50% for biogenic fuels while for MGO no data are available.

When using low-sulfur fuels (MGO, biogenic fuels), the emissions of particulate matter (PM) by mass is strongly reduced compared to HFO. This effect is of similar magnitude for all low-sulfur fuels of either fossil or biogenic origin. The reduction in PM mass emissions can be attributed primarily to the reduction in sulfate emissions, but also BC emissions are significantly lower. For all investigated fuels including HFO, emissions of PM and BC are strongest at low loading and decrease with higher loading.

Considering all investigated engine load conditions, PM emissions relative to HFO are reduced to 6−25% for MGO and to 6−60% for biogenic fuels. Reductions in BC relative emissions vary from 13% to 30% with MGO showing the strongest reduction to 13%, while soybean oil was found to emit significantly higher BC than the other low-sulfur fuels.

Despite PM emissions by mass are reduced when using low-sulfur fuels, emissions by number are significantly increased by a factor of 2 to four for biogenic fuels. In contrast, emissions of nonvolatile PM by number which are dominated by carbonaceous combustion particles are reduced similar to the reduction in BC mass emission. These two effects are connected since formation of new particles in the exhaust by nucleation/condensation is favored by the absence of the larger BC agglomerates (see next section) which may act as a sink for condensable gases.

PM emitted from biogenic fuels is composed almost entirely of carbonaceous matter like OM and EC; see Figure 2 for a comparison of relative chemical compositions for fuels HFO, palm oil, and animal fat. Sulfate and sulfate-associated water (see ref 5 for discussion) which dominate PM from HFO do not contribute to PM from biogenic fuels. Respective data on particle

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mass and number emissions for MGO are not available from this study but can be taken from ref 7.

4.2. Particle Size Distribution. Particle size distributions were measured from 5 nm to 1 μm in diameter for all fuels with the exception of MGO. Figure 3 shows particle number size distributions measured at engine loads of 10% and 100% for HFO as fossil reference fuel and palm oil as the biogenic fuel showing best combustion properties of all investigated fuels. Solid lines in Figure 3 represent fits of 4-modal log-normal distributions to the measured data. Respective modal parameters are summarized in
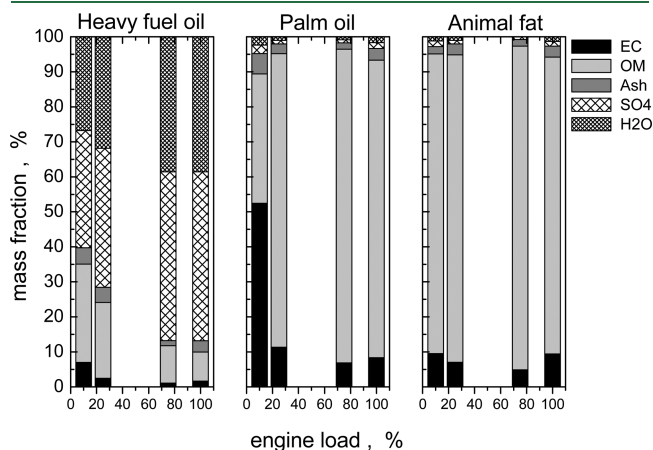
Figure 2. Fractional chemical composition of particulate matter emitted from a large diesel engine operating on fossil sulfur-rich heavy fuel oil (HFO) and on biogenic low-sulfur fuels palm oil and animal fat.
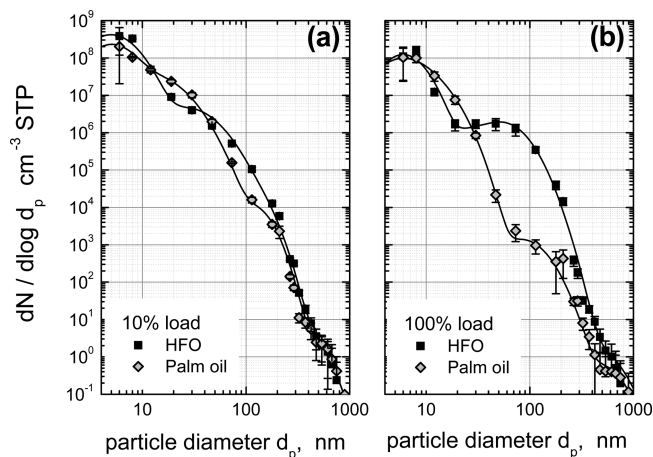

Figure 3. Particle number size distribution at 10% load (a) and 100% load (b) for HFO as the reference fuel and for palm oil representing biogenic fuels; particle size spectra were measured by DMA (d_p = 5 − 200 nm) and by OPC (d_p > 250 nm) instruments, and solid lines represent 4-modal log-normal size distributions fitted to the data.

Table 4. In the SI, additional data are shown in Figure SI4 which demonstrate the good reproducibility of size distribution measurements for the fuels under investigation.

Both exhaust aerosols are characterized by a strong nucleation particle mode (Mode 1) in the size range d_p < 10 nm. For palm oil, Mode 2 is centered at d_g = 13 nm, while the respective mode for HFO is centered at d_g = 25−27 nm. This mode likely contains primary BC particles. At 100% load the size distribution of HFO exhaust aerosol features a pronounced peak at d_g = 55 nm, while the size spectrum for biogenic fuels shows Mode 3 at d_g = 85 nm. In this particular size range, Mode 3 is reduced in number density by up to 2 orders of magnitude at 100% load and still by a factor of 2 at 10% load. Modes 3 and 4 are assumed to be made up of BC agglomerates.

The reduced soot particle mode coincides with a strong reduction in BC mass emission and in emissions of nonvolatile PM by number for biogenic fuels. The increased emission of total PM by number (see Figure 1) is mirrored in the exceedance of particle size spectra for biogenic fuels compared to HFO particularly for nucleation mode particles with d_p < 20 nm. Emissions of BC mass and particle number provide a consistent picture of the modification of PM emissions from marine diesel engines when switching from HFO to low-sulfur fuels of biogenic origin.

4.3. Fuel Life Cycle Analysis. The results of the fuel life cycle analysis including direct and indirect land use change are shown in Figure 4 in terms of emissions of CO_2 equivalents per kg of burned fuel. Respective data are given in Table SI1. Besides HFO, MGO, and biogenic fuels palm oil and soybean oil, Figure 4 also contains information on fossil fuels produced from oil sand (syncrude). For fossil fuels, CO_2 emissions per kg of fuel are enhanced by 15% compared to emissions during fuel burn if fuel life cycle effects are included in the emission budget. This value increases to 60% for syncrude. The CO_2 emission per kg of HFO including fuel life cycle effects is considered the reference case for our assessment.

Neglecting LUC effects, both soybean oil and palm oil show a positive CO_2 balance with respect to the reference HFO fuel life cycle analysis CO_2 emission value. Even if existing farmland is converted to energy plant production and indirect LUC is neglected, the balance compared to HFO is still positive. As soon as natural habitats such as savannah or tropical rainforest are converted to farmland, the overall CO_2 budget becomes clearly negative. If palm oil or soybean oil is produced on farmland with no associated LUC, a significant overall reduction in CO_2 emissions can be achieved. Producing palm oil on former tropical rainforest area or soybean oil on former savannah area increases overall CO_2 emissions by a factor of 2 compared to HFO use. Data for all investigated LUC are given in Table SI1.

The energy use for extraction and processing of syncrude and respective GHG emissions are significantly higher than for conventional crude oil,[30] while the downstream processing and direct emissions from the fossil energy carriers are similar to conventional
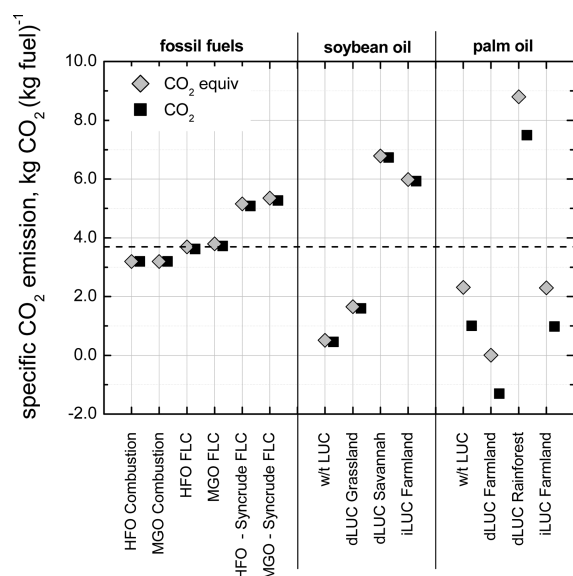
Table 4. Parameters of the 4-Modal Log-Norm Size Distributions

load, fuel	Mode #1			Mode #2			Mode #3			Mode #4		
	N, cm^{-3}	d_g, nm	σ_g	N, cm^{-3}	d_g, nm	σ_g	N, cm^{-3}	d_g, nm	σ_g	N, cm^{-3}	d_g, nm	σ_g
10%, HFO	2×10^8	5	1.55	2.5×10^6	27	1.67	3000	120	1.35	1.5	350	1.40
100%, HFO	5×10^7	6	1.45	4×10^5	25	1.45	8.5×10^5	55	1.50	0.8	500	1.50
10%, palm oil	1×10^8	5	1.50	1.7×10^7	13	1.68	3000	120	1.35	1.5	350	1.40
100%, palm oil	5×10^7	6	1.60	2.5×10^6	13	1.45	600	85	1.50	0.2	500	1.40

Figure 4. Greenhouse gas emissions in kg CO_2 per kg of burned fuel for HFO, MGO, soybean oil, and palm oil, calculated from a fuel life-cycle analysis (FLC) including direct and indirect land use change (LUC); CO_2 equivalents include non-CO_2 emissions during fuel production from, e.g., fertilization. The dashed line represents the fossil fuel reference case HFO FLC.

HFO and diesel. With syncrude-based fossil fuels currently being marketed mainly in Australia, Canada, and the USA, it is yet unclear which role syncrudes will play in the longer term in European crude imports. The EU regulation on GHG intensities of transport fuels used in the EU[31] requires a life cycle based net GHG reduction of all transport fuels of 7% by 2020, based on the 2010 emission levels. Canada as a key syncrude producer as well as smaller European producers especially in Estonia rigorously dispute the EU's power to restrict market access based on life-cycle GHG emissions, while environmental organizations call for a "ban" of syncrude. Thus, syncrude-based options should be seen as a sensitivity case indicating a possibly higher GHG intensity of future HFO and diesel in Europe, which in turn influences potential GHG benefits for biogenic fuels.

5. IMPLICATIONS

The aerosol indirect effect is the main pathway for the climate impact of PM emissions from shipping.[10,11] Since particulate sulfate forming from fuel sulfur is the main component causing humidity-related growth of combustion particles,[2,5] almost sulfate-free particles emitted from low-sulfur fuels will not undergo any substantial humidity growth.[5] Their ability to form cloud droplets is reduced and related indirect effects on climate are small.[1] Hence, particularly indirect effects of emitted PM should be reduced significantly when substituting high-sulfur HFO with low-sulfur fuels. Model studies using our emission data find that the modification of aerosol climate effects is of similar magnitude for low-sulfur fossil (MGO) as for biogenic fuels. For all low-sulfur fuels, the indirect effects are reduced by a factor of 3 to a value of -100 mW m^{-2}.[11]

Assessing long-lived climate effects requires the consideration of fuel life cycle analysis. Our results suggest that waste products like animal fat show a positive GHG balance because no additional production of biomass is required. Their overall availability is very

limited so that this application appears useful only in local power production. Soybean oil and palm oil have a large potential for GHG reduction. Palm oil achieves highest reductions if the conversion of tropical rainforest for growing palm trees is avoided. Producing energy plants on farmland with no or limited potential LUC allows a significant reduction in GHG emissions. However, a certification of sustainable biogenic fuel production is crucially needed.

■ ASSOCIATED CONTENT

S **Supporting Information.** Figures SI1—SI4 and Table SI1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: andreas.petzold@dlr.de.

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The units for columns 13 and 14 of Table 3 were changed in the version of this paper published November 17, 2011. The correct version published November 29, 2011.

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