

Fuel composition:

Fuel	C (w%)	H (w%)	S (w%)
MGO	87.80	13.10	0.01
LS-HFO	86.30	11.10	0.5

Table S 1 Main fuel components from MGO and HFO: carbon, hydrogen, and sulphur mass percentages.

Element / Analytical line (nm)	Elemental content (mg/kg)	
	MGO	LS-HFO
Al 308.215	< 1	7
As 189.042	< 1	< 1
Ba 233.527	< 1	1
Ca 315.887	< 1	4
Cr 267.716	< 1	< 1
Cu 327.396	< 1	< 1
Fe 259.941	< 1	12
K 766.491	< 1	-
Mg 279.553	< 1	< 1
Mn 257.611	< 1	< 1
Mo 202.095	< 1	1
Na 588.995	< 1	5
Ni 231.604	< 1	9
P 213.618	< 1	< 1
Pb 220.353	< 1	1
S 180.731	150	5060
Si 251.612	< 1	9
Sn 189.991	< 1	1
Ti 334.941	< 1	2
V 311.071	< 1	12
Zn 213.856	< 1	2

Table S 2 elemental composition of MGO and HFO (mg/kg)

	LS-HFO(g/kg)	MGO(g/kg)
SO ₂	3.63±0,41	0.79±0.19
THC	34.02±4,34	25.96±5.1

Table S3 The emission factor of total hydrocarbons (THC) and SO₂.

Input

Relative humidity	50%
Temperature	27°C
Residence time	70s

Table S4 Conditions within the PEAR and average residence time, used for KinSim simulations^{4,8}

	MGO	LS-HFO
O3	7.49±0.18 ppm	7.37±0.38 ppm
NO2	2.64±0.22 ppm	2.62±0.39 ppm
SO2	0.93±0.20 ppm	1.54±0.54 ppm
CO	1.54±0.34 ppm	2.24±0.38 ppm

Table S5 Note that SO2 in this case is the pear concentration of SO2 and THC combined.⁸ The value used for the KinSim calculations are the number given, the standard deviation was not included in the model run.

Output

Estimated exposure during MGO experiments

Molecules cm ⁻³ s	1.5 days	4.7 days	6.1 days	6.8 days	7.6 days	8.2 days	8.9 days
OH	1.24E+11	4.68E+11	6.68E+11	8.42E+11	1.11E+12	1.35E+12	1.57E+12
HO2	1.361E+12	7.18E+12	9.21E+12	1.04E+13	1.15E+13	1.21E+13	1.23E+13
NO	2.38E+11	3.34E+11	3.56E+11	3.68E+11	3.81E+11	3.89E+11	3.95E+11

Table S6 exposure calculated by KinSim for the MGO experiments based on input data.

Estimated exposure during LS-HFO experiments

Molecules cm ⁻³ s	1.5 days	3.3 days	6 days	7.4 days	8.7 days	8.5 days
OH	1.07E+11	2.72E+11	3.62E+11	6.15 E+11	9.41E+11	1.07E+12
HO2	1.66E+12	6.32E+12	8.52E+12	1.28E+13	1.57E+13	1.63E+13
NO	2.38E+11	3.15E+11	3.37E+11	3.73E+11	3.95E+11	4.01E+11

Table S7 exposure calculated by KinSim for the HFO experiments based on input data.

Photochemical age

LS_HFO				MGO		
UV Voltage	PTR-MS	KinSim		PTR-MS	KinSim	UV Voltage
0V	0	0		0	0	0V
2x3V	1.5±0.1	0.8		1.5±0.2	1.0	2x3V
4x3V	3.3±0.1	2.1		4.7±0.3	3.6	4x3.8V
4x3.8V	6.0±0.2	2.8		6.1±0.3	5.2	4x5V
4x6V	7.4±0.3	4.8		6.8±0.4	6.5	4x6V
4x8.8V	8.7±0.3	7.3		7.6±0.4	8.6	4x7.5V
4x10V	8.5±0.3	8.3		8.2±0.4	10.4	4x8.8V
				8.9±0.7	12.1	4x10V

Table S8 the photochemical age based on PTR-MS measurements and the KinSim age based on the UV voltage for both LS-HFO and MGO. All values are in OH equivalent days of age assuming OH concentration of 1.5×10^6 molecules cm⁻³ in the atmosphere

RO2 fate

MGO RO2 fate	1.5 days	4.7 days	6.1 days	6.8 days	7.6 days	8.2 days	8.9 days
HO2	59.5%	68.3%	66.2%	63.2%	61.3%	55.6%	52.4%
NO	6.1%	1.9%	1.6%	1.4%	1.2%	1.1%	1.0%
RO2-RO2	0.10%	0	0	0	0	0	0
OH	34.0%	29.7%	32.2%	35.4%	37.5%	43.3%	46.5%
Isomerization	0.30%	0.10%	0.10%	0.00%	0%	0.00%	0.00%

Table S9 The calculated RO2 fate of MGO based on the exposures from the KinSim calculated with the RO2 fate calculated.⁶

LS-HFO RO2 fate	1.5 days	3.3 days	6.0 days	7.4 days	8.7 days	8.5 days
HO2	65.7%	75.9%	76.5%	74.9%	71.0%	68.4%
NO	5.6%	2.3%	1.8%	1.3%	1.1%	1.0%
RO2	0.10%	0	0	0	0	0
OH	28.4%	21.7%	21.6%	23.8%	27.9%	30.5%
Isomerization	0.30%	0.10%	0.10%	0.00%	0%	0.00%

Table S10 The calculated RO2 fate of HFO based on the exposures from the KinSim calculated with the RO2 fate calculated.⁶

KinSim reactions

Reactant 1	Reactant 2	Product 1	Product 2	Product 3
O1D	H2O	OH	OH	
O1D	N2	O3P	N2	
O1D	CO2	O3P	CO2	
O1D	O2	O3P	O2	
O1D	O3	O2	O2	
O1D	O3	O2	O3P	O3P
O1D	H2	OH	H	
O3P	OH	O2	H	
O3P	HO2	OH	O2	
O3P	H2O2	OH	HO2	
O3P	O3	O2	O2	
H	O3	OH	O2	
OH	O3	HO2	O2	
HO2	NO	OH	NO2	
HO2	O3	OH	O2	O2
OH	HO2	H2O	O2	
H	HO2	OH	OH	
H	HO2	O3P	H2O	
H	HO2	O2	H2	
OH	H2	H2O	H	
OH	OH	H2O	O3P	
NO	O3	NO2	O2	
NO2	O3	NO3	O2	
OH	H2O2	H2O	HO2	

O1D	N2O	NO	NO	
HO2	NO2	HNO4		
OH	HNO4	H2O	O2	NO2
O1D	N2	N2O		
OH	NO2	HNO3		
O3P	O2	O3		
H	O2	HO2		
OH	OH	H2O2		
OH	SO2	HSO3		
HSO3	O2	HO2	SO3	
OH	HNO3	H2O	NO3	
O2	HV185	O3P	O3P	
O3	HV254	O2	O1D	
H2O2	HV185	HO2	H	
H2O2	HV254	OH	OH	
HO2	HV254	OH	O1D	
HO2	HV185	OH	O1D	
H2O	HV185	OH	H	
HO2	HO2	H2O2	O2	
O3P	NO	NO2		
O3P	NO2	NO	O2	
O3P	NO2	NO3		
O3P	NO3	O2	NO2	
OH	NO	HNO2		
OH	HNO2	H2O	NO2	
HO2	NO3	OH	NO2	O2
NO2	NO3	NO	NO2	O2
NO2	NO3	N2O5		
NO3	NO3	NO2	NO2	O2
O3	HNO2	O2	HNO3	
N2O5	H2O	HNO3	HNO3	
NO2	HV185	NO	O1D	
NO2	HV254	NO	O3P	
NO3	HVVIS	NO2		
N2O	HV185	N2	O1D	
HNO4		NO2	HO2	
N2O5		NO2	NO3	
N2O	O1D	N2	O2	
N2O	O1D	NO	NO	
N2O	OH	N2	HO2	
N2O	HV185	N2	O1D	
NH3	HNO3	NH4NO3		
NH3	OH	H2O	NH2	
NH2	NO	N2	H2O	
NH2	NO	N2H	OH	
NH2	NO	N2	H	OH
NH2	NO2	N2O	H2O	
NH2	NO2	N2	H2O2	
NH2	NO2	H2NO	NO	
CO	OH	HOCO		

CH4	OH	CH3	H2O	
CH3	O2	CH3O2		
CH3O2	NO	CH3O	NO2	
CH3O	O2	HCHO	HO2	
HCHO	OH	HCO	H2O	
HCO	O2	CO	HO2	
C2H6	OH	C2H5	H2O	
C2H5	O2	C2H5O2		
CH2OH	O2	CH2O	HO2	
C2H5O2		C2H5O		
OH	NO3	HO2	NO2	
CO	OH	CO2	H	
HOCO	O2	HO2	CO2	
H2O2	H	H2	HO2	
CH3	H2O2	CH4	HO2	
HSO3	O2	HO2	SO3	

Table S11 All reactions that were added to the KinSim. Reaction rates used can be supplied upon request.

Van-Krevelen regression line coefficients

Fit of Fuel (days-days)	a	b	R ²
MGO (0-4.7)	1.7976±0.0195	-0.97355±0.0802	0.973604
MGO (4.7-8.9)	1.6145±0.0151	-0.54266±0.0237	0.990584
HFO (0-3.3)	1.7373±0.00739	-0.89447±0.0447	0.98285
HFO (3.3-8.7)	1.6302±0.0108	-0.54077±0.0167	0.994284

Table S12 The Van Krevelen plot regression lines fitted to a straight-line $y=a+bx$.

Particle size and number

LS-HFO			MGO		
age(days)	GMD(nm)	cm ⁻³	GMD(nm)	cm ⁻³	age(days)
0	94.4±2,8	3.30E+06	75.1±6,1	1.83E+06	0
ozone	91.4±5,5	3.62E+06	77.1±9,9	3.07E+06	ozone
1.5	32.4±2,2	4.00E+07	33.1±5,3	2.68E+07	1.5
3.3	37.1±0,7	8.10E+07	36.3±1,0	7.82E+07	4.7
6	44.3±0,9	1.02E+08	36.0±0,4	8.81E+07	6.1
7.4	42.8±2,1	1.35E+08	35.4±1,4	9.59E+07	6.8
8.5	46.5±0,5	1.24E+08	36.0±0,7	9.77E+07	7.6
8.7	46.6±0,8	1.22E+08	35.6±0,4	1.04E+08	8.2
			35.3±0,6	1.14E+08	8.9

Table S13 SMPS data for each aging point of both LS-HFO and MGO. GMD being the geometric mean diameter based on particle number

LS-HFO			MGO		
age(days)	$\frac{EF_{AMS}}{EF_{smgs}}$	$\frac{EF_{AMS}}{EF_{smgs} - EF_{eBC}}$	$\frac{EF_{AMS}}{EF_{smgs}}$	$\frac{EF_{AMS}}{EF_{smgs} - EF_{eBC}}$	age(days)
0	0.50±0.06	1.08±0.24	0.25±0.03	0.47±0.09	0
ozone	0.45±0.05	0.86±0.17	0.29±0.03	0.48±0.09	ozone
1.5	0.74±0.09	1.01±0.16	0.70±0.08	0.90±0.13	1.5
3.3	0.77±0.09	0.94±0.13	0.46±0.05	0.52±0.07	4.7
6	0.88±0.10	1.05±0.14	0.48±0.06	0.54±0.07	6.1
7.4	0.82±0.10	0.94±0.12	0.51±0.06	0.57±0.07	6.8
8.5	0.82±0.10	0.94±0.13	0.47±0.06	0.52±0.07	7.6
8.7	0.82±0.10	0.92±0.12	0.47±0.06	0.52±0.07	8.2
			0.48±0.06	0.52±0.07	8.9

Table S14 comparison of the observed mass in AMS compared to SMPS and SMPS minus black carbon, for both LS-HFO and MGO.

LS-HFO			MGO		
age(days)	g/kg	g/kWh	g/kg	g/kWh	age(days)
0	2.05 ±0.51	0.60±0.15	0.78±0.24	0.20±0.06	0
ozone	1.89±0.45	0.56±0.13	0.85±0.31	0.22±0.08	ozone
1.5	3.18±1.01	0.93±0.30	1.60±0.46	0.41±0.11	1.5
3.3	5.12±1.11	1.50±0.33	3.30±0.66	0.83±0.17	4.7
6	7.48±1.63	2.19±0.48	3.50±0.64	0.88±0.16	6.1
7.4	8.79±2.20	2.58±0.64	3.66±0.87	0.93±0.22	6.8
8.5	9.65±2.13	2.83±0.63	3.75±0.73	0.95±0.19	7.6
8.7	9.59±2.08	2.81±0.61	3.82±0.70	0.96±0.18	8.2
			4.16±0.94	1.05±0.24	8.9

Table S15 total particle mass emission factors for LS-HFO and MGO as both aerosol mass per kg of fuel and aerosol mass per kWh.