

Article

Application of upgraded drop-in fuel obtained from biomass pyrolysis in a spark ignition engine

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Supplementary data

S.1 PAH analysis

The following PAH (naphthalene (Np), acenaphthylene (Acy), acenaphthene (Ace), phenanthrene (Phe), anthracene (An), 2+2/4-methylphenanthrene (2+2/4MePhe), 9-methylphenanthrene (9MePhe), 1-methylphenanthrene (1MePhe), 2,5-/2,7-/4,5-dimethylphenanthrene (DiMePhe), fluoranthene (Flt), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[j]fluoranthene (BjF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) and coronene (Cor) were quantified using gas chromatography mass spectrometry mass spectrometry (GC-MS-MS).

Briefly, the filter and the resins were extracted individually by Soxhlet with dichloromethane (DCM) after the addition of a deuterated standard solution (Ace-d₁₀+An-d₁₀+BaA-d₁₂+BaP-d₁₂+BghiP-d₁₂) for 24 hours. Samples were concentrated by a rotary evaporator and afterwards by a nitrogen stream flow until 1 mL. Concentrated samples were cleaned through a silica gel column (1 g, pre-cleaned by Soxhlet with DCM and heated for at least 1 hour at 150°C) with Na₂SO₄ anhydrous at the top. The column was eluted/conditioned with 10 mL DCM before addition of the sample. The concentrated raw extract was loaded on top of the column and the sample was eluted with 15 mL of DCM. After elution, sample was further concentrated in a pure N₂ stream. The solvent was exchanged to n-hexane and p-terphenyl native was added as recovery standard keeping a final volume of 1 mL.

Each PAH compound was quantified by GC-MS-MS operating at electron impact energy of 70 eV and using multiple reaction monitoring (MRM) and MS/MS modes for the ion preparation according to Table S3. A Varian Select PAH capillary column (30 m × 0.25 mm internal diameter × 0.25 μm film thickness) was used to quantify PAH and 1 μL of sample was injected in splitless mode. The GC conditions were: 1.5 mL/min Helium flow; temperature-time programme: 70°C, 1 min, increasing 10°C/min till 325°C and isotherm for 13.5 minutes. The injector temperature was set to 280°C, the transfer line to 300°C and the ion trap to 200°C. The identification and PAH quantification were done according to retention times with standard solutions and the internal standard method relative to the closest eluting PAH surrogate.

The PAH quantification was performed by the internal standard method. PAH calibration curves were prepared (5/50-900 ng/ml) and the relative response factors (RRF) of the individual PAH were used to calculate the mass for each compound. For each individual PAH coefficients of determination were $R^2 > 0.99$.

Concentration of PAH in the combustion samples below the detection limit were considered as non-detected (N.D.) and those with concentrations between the detection limit and quantification limit were considered as below the quantification limit (<L.Q.) and they were not quantified.

Quality control

Blank filters and resins after the addition of a deuterated PAH sample were individually extracted and the same protocol than the combustion samples was performed. The average blank concentration was subtracted from each sample to correct for the whole extraction and analysis procedures. The method detection limits were calculated by analyzing blank filters for particulate PAH and XAD-2 resins for gas-phase PAH after applying the same protocol than combustion samples. Limits of detection were calculated as three times the standard deviation of the blank filters and resins, respectively. The instrument detection limits were also determined by analyzing several replicates of a low concentration PAH standard (5 ng/ml)

Respective values of relative standard deviations (RSD) for the relative response factors of the calibration curves were always lower than 30% fulfilling the criterion suggested by EPA (EPA/625/R-96/010b Compendium of methods for the determination of toxic organic compounds in ambient air Second Edition Compendium Method TO-13A Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS) Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268 January 1999).

Table S1. Composition conditions for PAH quantification by GC-MS-MS

Name	Abbreviation	Precursor ion	Quantification ion	CID excitation amplitude ^a (V)	Excitation RF storage level ^b (m/z)	Emission current (μA)	Ion preparation
Napthalene	Np	128	102	0.90	60	80	MS-MS
Acenaphthylene	Acy	152	150	1.30	75	80	MRM
Acenaphthene-d ₁₀	Ace-d ₁₀	162	160	0.60	75	80	MRM
Acenaphthene	Ace	153	151	1.50	75	80	MRM
Fluorene	Fl	165	163	1.50	75	80	MS-MS
Phenanthrene	Phe	178	152	1.20	75	80	MRM
Anthracene-d ₁₀	An-d ₁₀	188	160	0.90	75	80	MRM
Anthracene	An	178	152	1.20	75	80	MRM
2+2/4-Methylphenanthrene	2+2/4MePhe	191	189	0.60	75	80	MS-MS
9-Methylphenanthrene	9MePhe	191	189	0.60	75	80	MS-MS
1-Methylphenanthrene	1MePhe	191	189	0.60	75	80	MS-MS
2,5-/2,7-/4,5-Dimethylphenanthrene	DiMePhe	206	191	0.90	75	80	MS-MS
Fluoranthene	Flt	202	200	1.80	75	80	MS-MS
Pyrene	Py	202	200	1.80	75	80	MS-MS
p-terphenyl	p-tph	230	215	1.40	75	80	MRM
Benzo(a)anthracene-d ₁₂	BaA-d ₁₂	240	236	2.10	85	80	MRM
Benzo(a)anthracene	BaA	228	226	2.60	85	80	MRM

Chrysene	Chry	228	226	2.60	85	80	MRM
Benzo(b)fluoranthene	BbF	252	250	2.00	90	80	MS-MS
Benzo(k)fluoranthene	BkF	252	250	2.00	90	80	MS-MS
Benzo(e)pyrene	BeP	252	250	2.20	90	90	MRM
Benzo(a)pyrene-d ₁₂	BaP-d ₁₂	264	260	2.80	90	90	MRM
Benzo(a)pyrene	BaP	252	250	2.20	90	90	MRM
Indeno(1,2,3-cd)pyrene	IcdP	276	274	3.30	90	90	MRM
Dibenzo(a,h)anthracene	DahA	278	276	3.30	90	90	MRM
Benzo(ghi)perylene-d ₁₂	BghiP-d ₁₂	288	284	3.70	90	90	MRM
Benzo(ghi)perylene	BghiP	276	274	3.50	90	90	MRM
Coronene	Cor	300	298	3.90	90	90	MS-MS

^a Amplitude of waveform applied during CID of precursor ion.

^b RF voltage in m/z units used during excitation of precursor ion.

MRM= multiple reaction monitoring mode

Table S2. PAH compounds and their toxic equivalency factors (TEF).

PAH compound	Nisbet and LaGoy (1992)[1]
Np	0.001
Acy	0.001
Ace	0.001
Fl	0.001
Phe	0.001
An	0.001
2+2/4MePhe	0.001 ^a
9MePhe	0.001 ^a
1MePhe	0.001 ^a
DiMePhe	0.001 ^a
Flt	0.001
Py	0.001
BaA	0.1
Chry	0.01
BbF	0.1
BkF	0.1
BeP	0.01
BaP	1
IcdP	0.1
DahA	1
BghiP	0.01
Cor	0.001 ^b

^a due to similarity in the structure it was taken the same TEF than phenanthrene

^b TEF for coronene according to Malcolm and Dobson (1994)[2]).

References

- [1] I.C.T. Nisbet, P.K. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regulatory Toxicology and Pharmacology*, 16 (1992) 290-300.
- [2] H.M. Malcolm, S. Dobson, B. Great, P. Her Majesty's Inspectorate of, S. Monks Wood Experimental, The calculation of an Environmental Assessment Level (EAL) for atmospheric PAHs using relative potencies, (1994).