Chromium as a Potential Catalyst in the Thermal Formation of Chlorinated Aromatic Compounds

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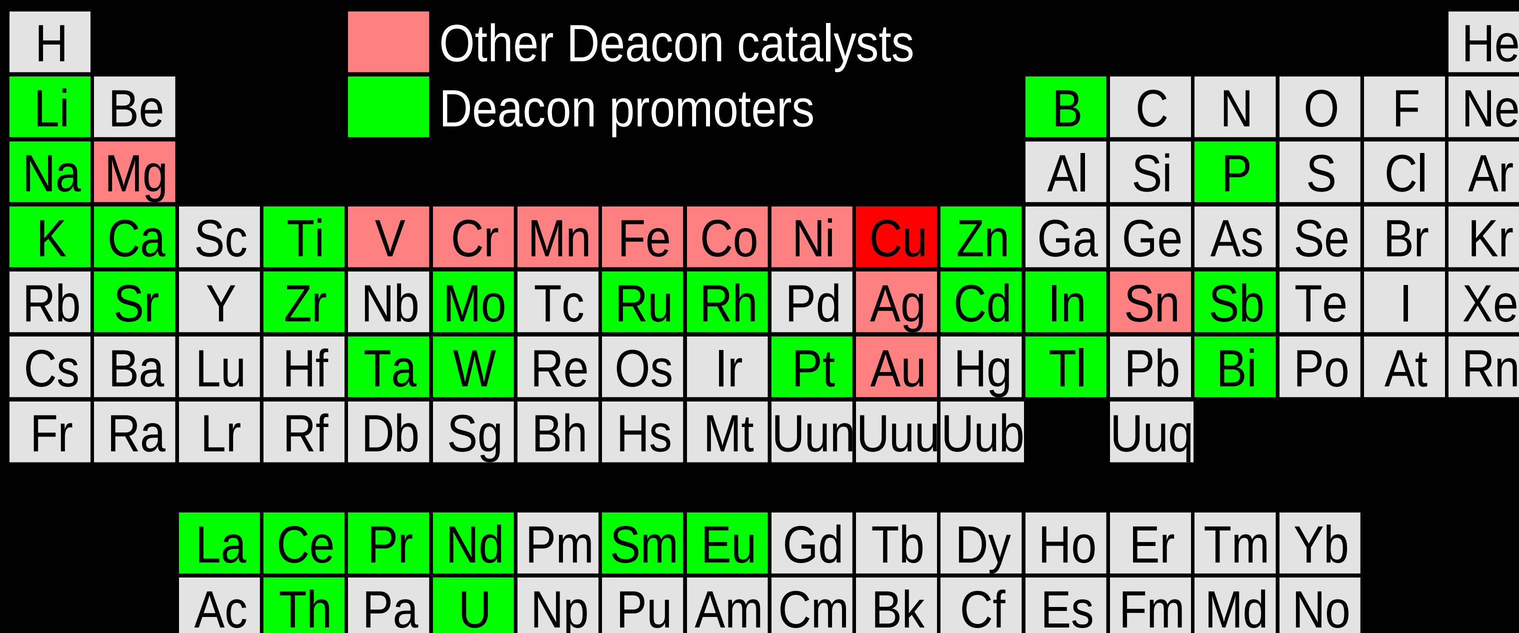
Aim and Scope

- The thermal formation of chlorinated aromatic compounds is catalyzed by fly ash components
- Much interest has focussed on the role of copper, but what is the role of other metals?
- Here we will attempt to re-evaluate the analytical results from a series of 16 trial burns with different waste fuels
  - These trial burns were originally performed to evaluate other combustion characteristics

The Deacon Reaction

- Postulated to be responsible for the low temperature formation of chlorinated aromatics
  - $2HCl + \frac{1}{2}O_2 \leftrightarrow H_2O + Cl_2$
  - Catalyzed by copper, but also by a number of other transition metals
- It is therefore of interest to widen the scope to include the fly ash composition as a whole

A substantial portion of the periodic table



Materials and Methods

- Trial burns with different waste fuels in a 20 MW bio-fuel incinerator
- Fractions of waste from
  - Households (separated at source)
  - Specified industrial wastes
  - Waste from forestry (reference fuel)
- Fly ash samples analyzed for content of
  - 32 elements
  - 16 chlorinated phenols (di-penta)
  - 11 chlorinated benzenes (di-hexa)
  - 25 PCDD/PCDF (2378-substituted congeners and homologous groups)

Chemical Analysis

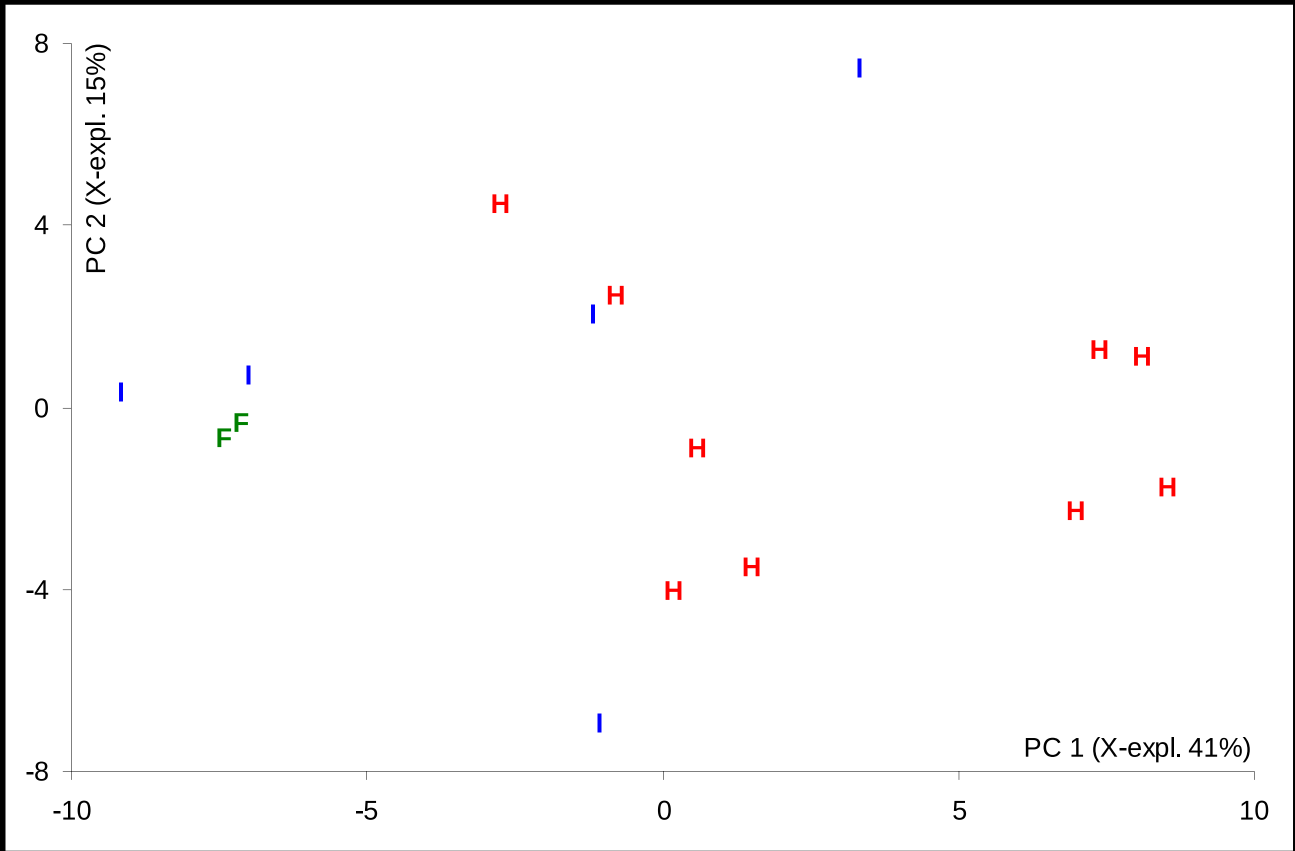
- Sampling
  - –Grab samples of fly ash from electrostatic precipitator twice every hour (24 h test)
  - –After mixing, one composite was analyzed
- Analysis
  - –AAS: Pb, Cd and Hg
  - –XRF: Other minerals and trace elements
  - –HRGC-MS/SIM: Chlorinated benzenes, phenols, PCDD and PCDF [1]

[1] Öberg, T; Warman, K.; Bergström, J. Chemosphere **1987**, *16*, 2451

Data Analysis

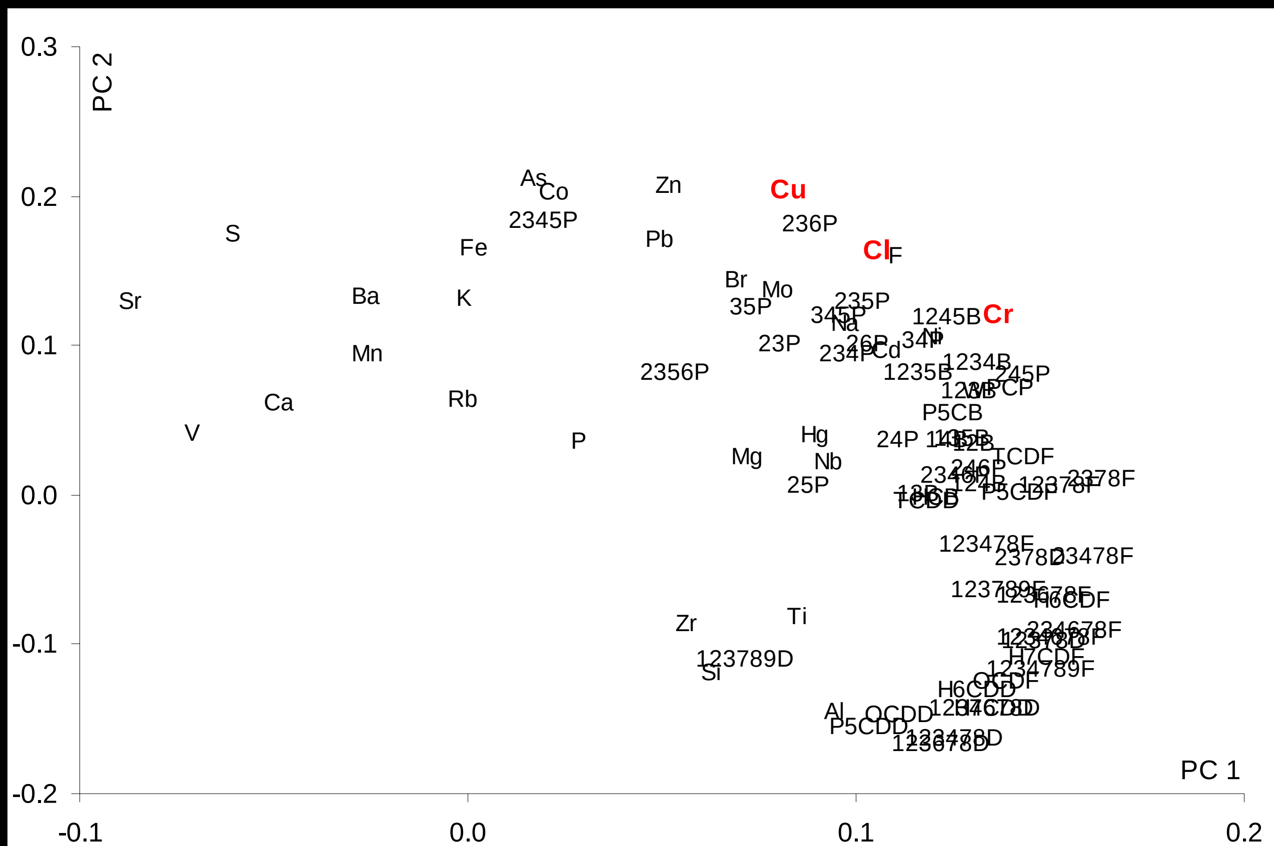
- The correlation pattern was evaluated using principal component analysis (PCA)
- Values below the detection limit were treated as missing
- Each analytical variable was transformed to normality employing a modified Box-Cox power transformation: $y = (Y^{\lambda}-1)/\lambda$
- All variables were standardized to zero mean and unit variance before the data analysis

The PCA Model



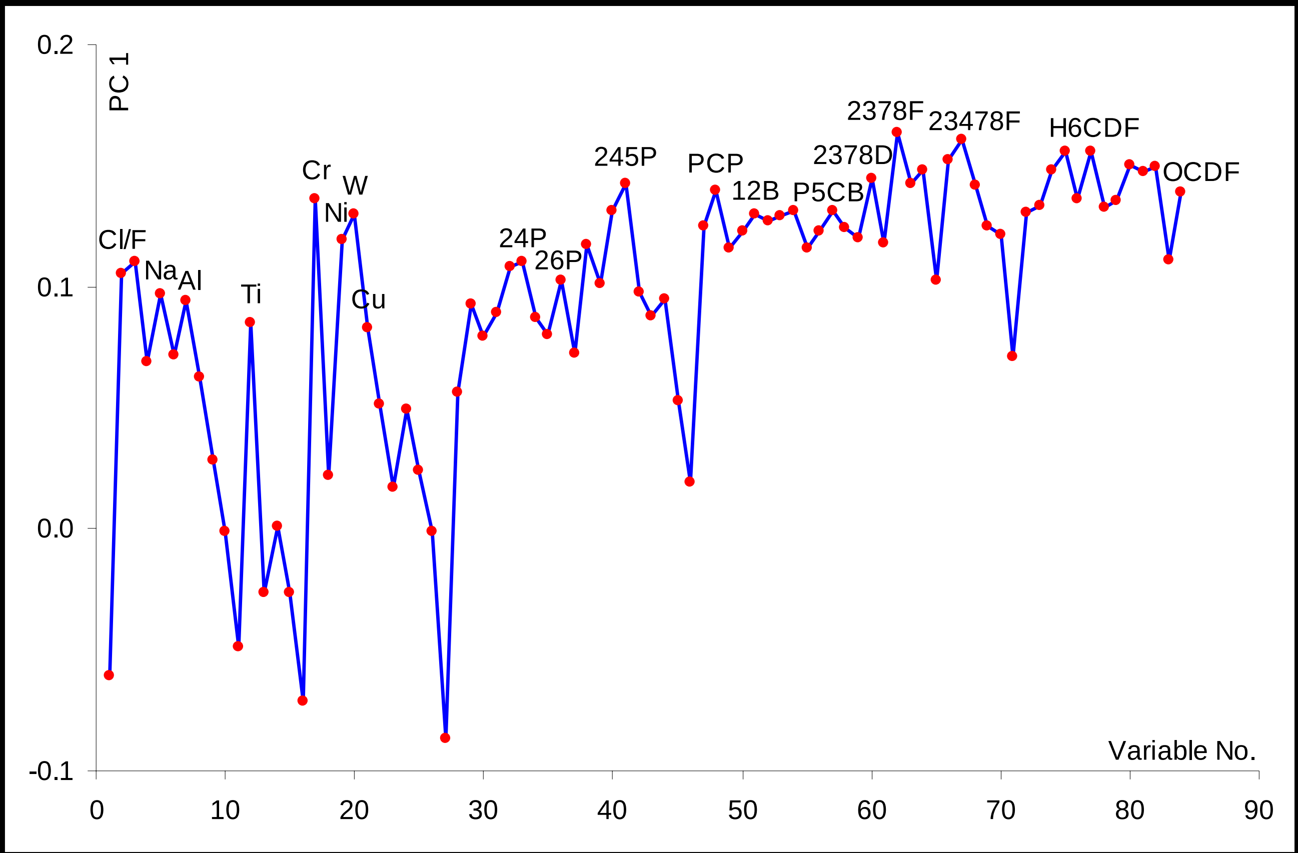
Two significant components as determined by cross-validation, explains 56% of the variance. Sorted household, industrial and forestry waste denoted as H, I and F in the scores plot

The Correlation Pattern



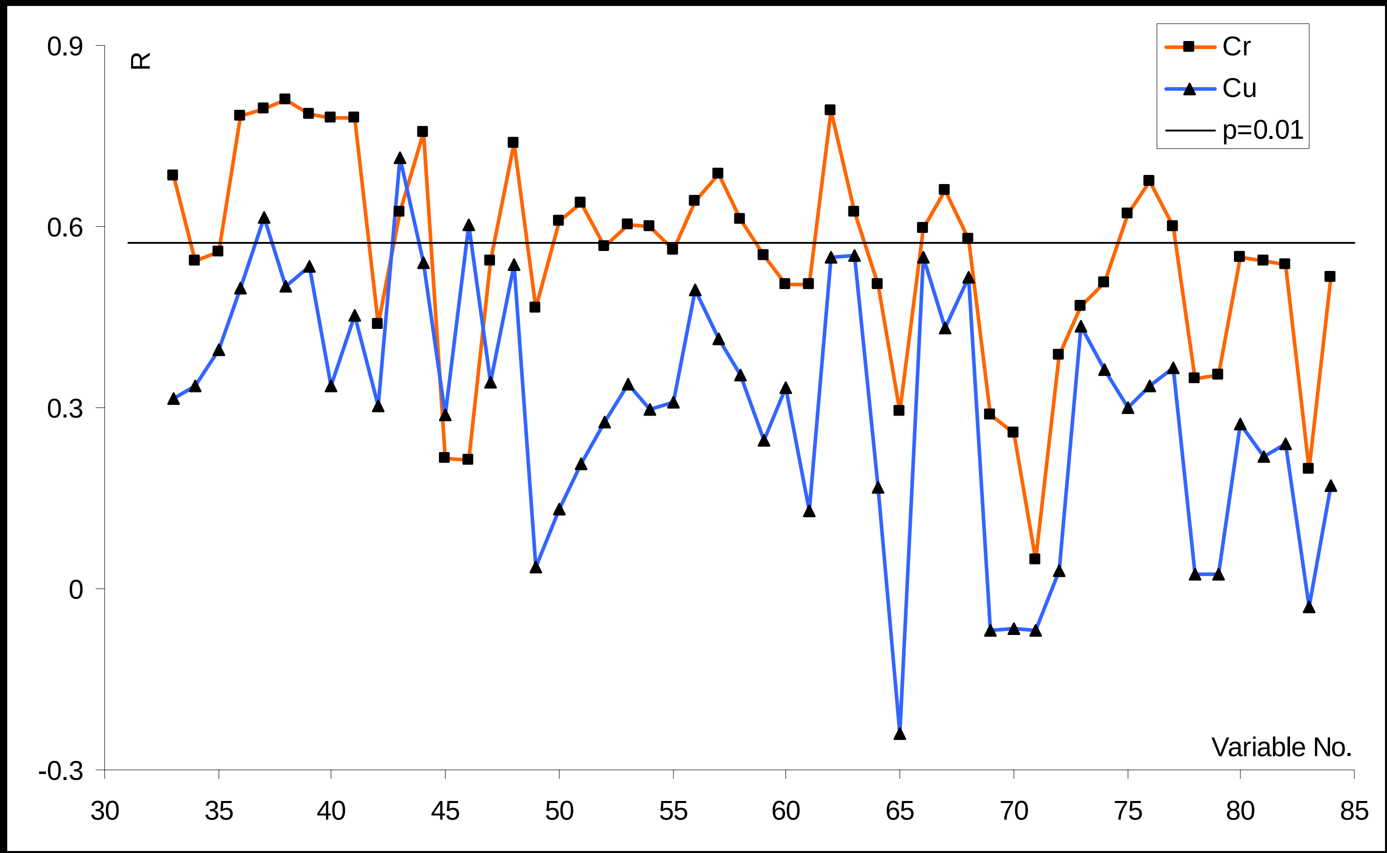
Variable loadings along the first two components of the PCA model. Copper, chlorine and chromium are highlighted

Major Contributions



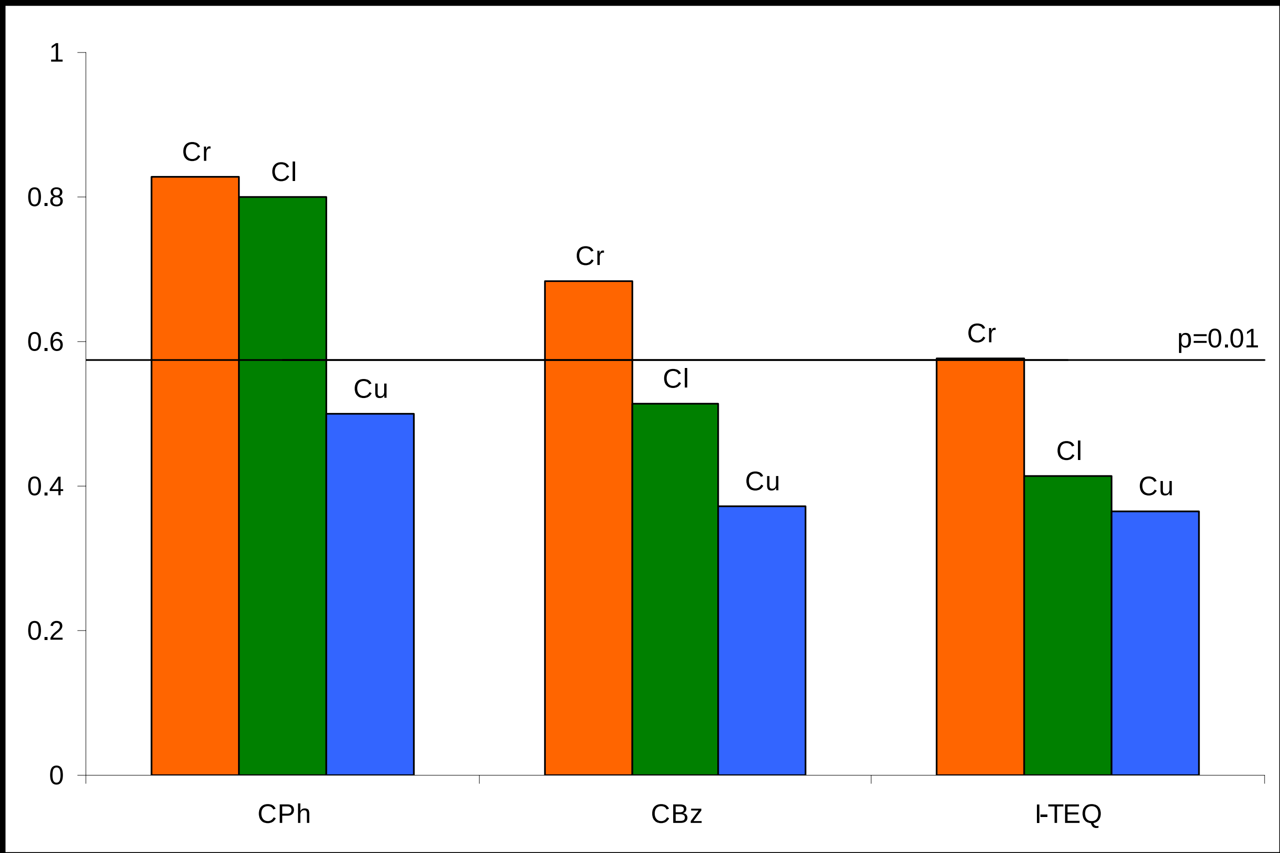
Variable loadings along the first principal component. Major contributions from Cr, Ni, W and many 2378-substituted PCDF

Correlation Coefficients



Chlorophenols nos 33-48, chlorobenzenes nos 49-59 and PCDD/F nos 60-84

Correlation, cont.



Correlation coefficients between each group of chlorinated aromatics and chromium, chlorine and copper

Comparison

- Significant correlations ($p=0.01$)
  - Cr (25), W(14), Ni (9), Cl (8), Cu (3)
- Concentrations
  - The fly ash concentrations of both nickel and tungsten are low (~10-100 µg g^{-1}) compared to chromium and copper (~200-2000 µg g^{-1})
- Deacon catalysts
  - Chromium has a high activity
  - Nickel is a much weaker catalyst
  - Tungsten can act as a promoter

Hypothesis

- *Transition metals other than copper are of equal importance in the catalytic activity of fly ash*
- *Chromium is high on this "candidate list"*

- Relative activities
  - $NiCl_2 < MnCl_2 < FeCl_3 < CuCl_2 < CrCl_3$ [1]
  - Cr_2O_3 was patented as a Deacon catalyst in 1947 [2]
- Sufficiently small enthalpies [3], of HCl absorption and oxidation (ΔH at 298 K)
  - Exothermic, e.g. $Cr_2O_3 + 2HCl \rightarrow 2CrOCl + H_2O + 20.5$ kJ
  - Endothermic, e.g. $2CrOCl + ½O_2 \rightarrow Cr_2O_3 + Cl_2 - 6.3$ kJ
- At least one previous study report on the correlation between chromium and chlorinated aromatics [4]

[1] Todo *et al.* 1966 cited by Allen, J. A.; Clark, A. J. Rev. Pure Appl. Chem. **1971**, *21*, 145

[2] B.P. 584,790 cited by Allen, J. A. J. Appl. Chem. (London) **1962**, *12*, 406

[3] Hishham, M. W. M.; Benson, S. W. J. Phys. Chem. **1995**, *99*, 6194

[4] Manninen, H. *et al.* Environ. Sci. Pollut. Res. **1996**, *3*, 129

Future work

- We suggest that a strategy centred on statistical design of experiments be applied to test the hypothesis put forward
  - to quantify the relative importance

  and
  - interactions of different waste fuel components
- Experiments both in the laboratory and in full-scale combustion plants are needed

Acknowledgements

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Öberg, T., Öhrström, T., Bergström, J. Environ. Chem. 2004, 1, 18