

# Towards an effective control of trace emissions from agricultural waste combustion: fly ash characterization versus thermodynamic modelling.

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CLEANBIOM project aims to a sustainable management and operation of decentralized medium-scale plants (1-50 MWth) for the combustion of typical Mediterranean Basin annual biomasses. The Medium Combustion Plant Directive (EU Directive 2015/2193) set emission limit values although enforces a surveillance plan of quite a low frequency (every 3 years). In the meanwhile, the consequences of such a lack of emissions records, in terms of a rationale for control operation could be fulfilled by robust predicting tools, such as thermodynamic modeling.

## Methods

The field study was performed in a bubbling fluidized bed combustion plant (1 MW nominal output) equipped with a Hybrid Filter, which integrates electrostatic precipitator (ESP) and bag filter (BF), as described in detail by (Aragon, 2015; Sanz, 2012).

Five 1-week experiments were carried out, using olive prune chips, with variable operation conditions (sieved/non-sieved, combustion air temperature and primary/secondary air distribution). Raw aerosol samples were collected and analyzed by X-Ray Diffraction (XRD). MTDATA v5.01 was used for thermodynamic equilibrium calculations. Input data were the fuel elemental composition and bed operating temperature.

## Results

Figure 1 shows the results for the most abundant crystalline species in all tests. All samples present the same common species with some differences in the relative abundance.

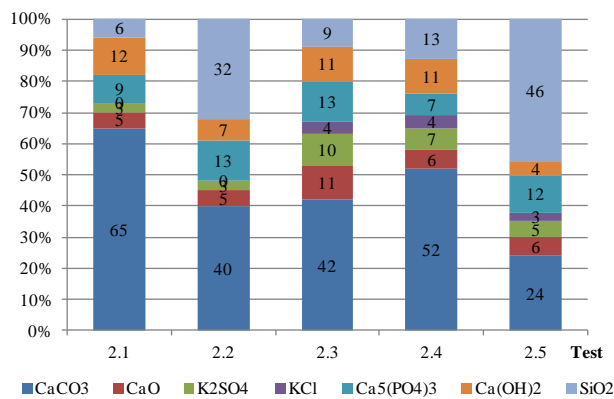


Figure 1. Relative abundance of fly ash crystalline species in raw aerosol (by XRD analysis).

Table 1 includes the thermodynamic prediction results for some relevant elements. Sulfur is present as a single species ( $K_2SO_4$ ), the most part of calcium forms silicates, potassium is mainly present as phosphate and sulfate compounds. Finally, silica distributes the most, combining primarily with alkaline earth elements.

Compared to experimental results,  $K_2SO_4$  is the only phase predicted by the model.  $KCl$  is supposed to condense at lower temperatures. Predicted silica phases most probably are present in the amorphous phase, not distinguishable by XRD.

Table 1. S, Ca, K and Si molar partitioning prediction in solid species for Test 2.1 at bed temperature, as obtained by chemical equilibrium modeling.

T (K)	S	Ca	K	Si
Bed	100%	57,08%	48,74%	61,90%
1040	$K_2SO_4$	$MgCa_3(SiO_4)_2$	$K_3PO_4$	$MgCa_3(SiO_4)_2$
		29,57%	45,93%	24,05%
		$Ca_2SiO_4$	$K_2SO_4$	$Ca_2SiO_4$
		10,84%	5,16%	8,82%
		$Al_2Ca_2SiO_7$	$AlKSiO_4$	$Al_2Ca_2SiO_7$
		1,82%	0,16%	2,11%
		$CaFe_2O_4$	$K_2CrO_4$	$AlKSiO_4$
		0,69%	0,01%	1,68%
		$Ca_4Ti_3O_{10}$	$K_3AsO_4$	$Al_2Na_2Si_6O_{16}$
				1,23%
				$Na_2SiO_3$
				0,17%
				$Sr_2SiO_4$
				0,04%
				$Ba_2SiO_4$

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Aragon, G. et al (2015) *Energy & Fuels* **29**, 2358-2371

EU directive 2015/2193 on the limitation of emissions of certain pollutants into the air from medium combustion plants.

Sanz, D. et al (2012) *European Aerosol Conference 2012* P038.