Reduction of particle emissions by using additives

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Additives

Additives can be used to decrease

- Sintering/slagging of fuel bed
- Bed agglomeration
- Deposit formation and subsequent corrosion
- Particle emission

Formation of fine particles is hindered by capturing of K in non (less)-volatile compounds => K stays in the bottom ash.

*Therefore, this presentation is focused on **fuel additives** – additives in a fuel mix and additives mixed with the fuel*

Outline

1. Background: Some ash basics
2. Additives
   - Calcium
   - Phosphorus
   - Aluminium
   - Aluminium-silicate
3. Case study ”Combustion of straw pellets with kaolin as additive”
   - Experimental
   - Results
   - Conclusions
4. Summary

1. Background: Some ash basics

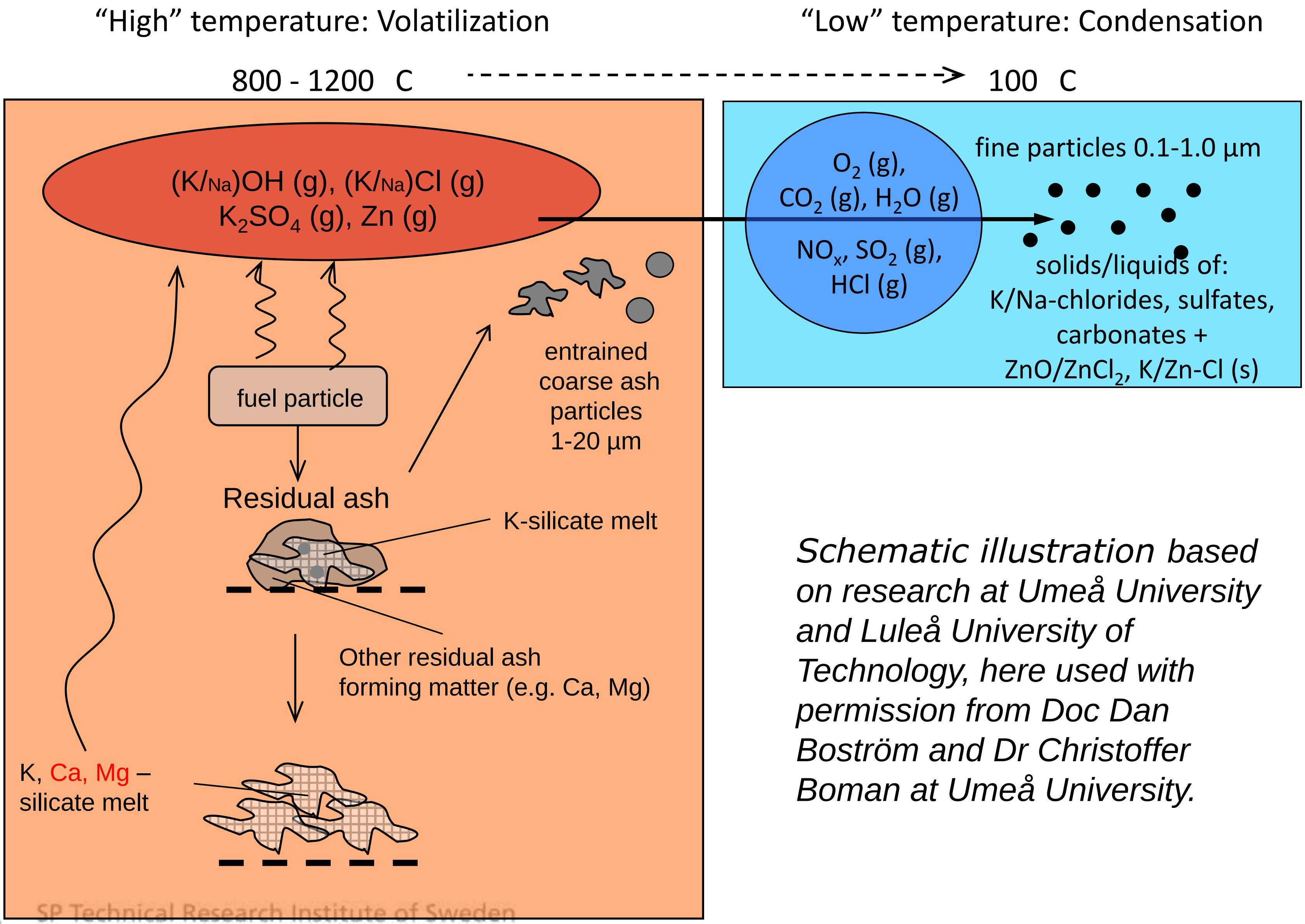
Ash elements important for the particle emission

Examples Ash-rich biomass

Woody fuels	Wood pellets	Wood briquettes	Bark pellets	Oat grain	Forest residue
Moisture (mass-% wet)	7.6	8.8	7.8	11	15.8
Ash (mass-% dry fuel)	0.4	0.3	3.7	3.1	3.2
Ultimate analysis (mass-% dry fuel)					
C	49.9	49.9	52.1	47.6	50.8
O	43.4	43.4	37.8	40	39.4
H	6.2	6.2	5.9	6.6	6
N	0.05	0.09	0.48	2.2	0.66
S	<0.01	<0.01	0.03	0.19	0.04
Cl	<0.01	<0.01		0.05	0.02
Lower heating valu (MJ/kg dry fuel)	19.1	18.8	20.1	18.5	19.2
Ash composition (mass-% dry fuel)					
Ca	0.09	0.06	-	0.10	0.49
K	0.04	0.04	-	0.57	0.20
Si	0.02	0.01	-	0.25	0.51
Mg	0.01	0.01	-	0.14	0.08
Mn	0.01	0.01	-	0.01	0.07
Fe	0.007	0.001	-	0.01	0.04
P	0.006	0.006	-	0.44	0.05
Al	0.003	0.001	-	0.02	0.09
Na	0.002	0.001	-	0.01	0.05
Ba	0.001	0.001	-	0.01	0.01
Zn	0.001	0.001	-	0.01	0.01
Ti	0.0002	0.0001	-	0.01	0.004

The relative concentrations of K, Ca, Si and P decides whether K leaves the fuel bed and forms particles.

General ash transformation in woody biomass (Si-dominated)

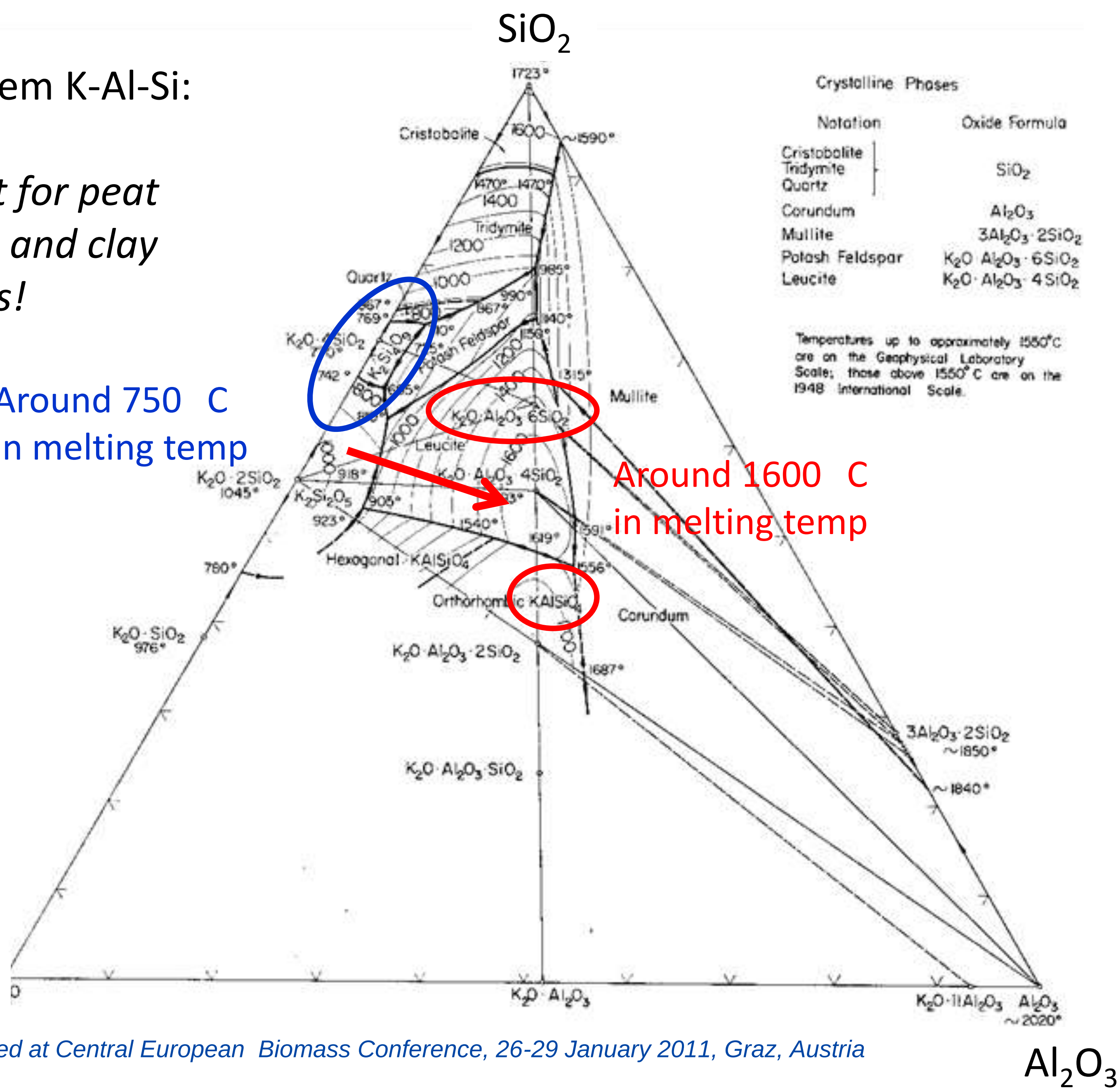


Schematic illustration based on research at Umeå University and Luleå University of Technology, here used with permission from Doc Dan Boström and Dr Christoffer Boman at Umeå University.

Ash –The influence from adding Aluminium

The system K-Al-Si:

Relevant for peat addition and clay additives!



2. Additives

Additives

Additives can be sorted into some main groups, depending of their chemical composition:

1. Calcium
2. Phosphorus
3. Sulphur
4. Aluminium
5. Aluminium-silicate

Relevant for reduction of particle emissions

Calcium

Commonly used as an additive to reduce acidic gases, but only limited investigated as additive to reduce particle emissions.

- $Ca(OH)_2$
- Limestone (dominated by the mineral calcite), calcite $CaCO_3$

Si-rich fuel, *e.g.* straw or woody fuels

Ca-additive have shown no effect on fine particle emissions since the formation of Calcium-Potassium-Silicates not reduce the initial formation of K-Silicates (potential increase in coarse PM though)

P-rich fuels, *e.g.* oat grain

Ca-additive may prevent particle emissions by formation of Ca/Mg-K-Phosphates which are less volatile than pure K-Phosphates

Important to supply calcium additives early in a boiler, *e.g.* with the fuel

Introducing Ca also have positive (reducing) effects on slagging - it promotes the formation of high temperature melting Ca-K-Silicates and –Phosphates.

Phosphorus

Scarcely studied as an additive.

- Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$
- Phosphoric acid
- Sewage sludge (high content of P)

Fine particle emissions may be reduced by capturing K into high-temperature melting compounds, *i.e.* Ca-K-Phosphates. Ca-K-Phosphates are less volatile than K-Phosphates that otherwise will form. Detailed mechanisms only partly understood.

The specific combination of fuel/additive mixture will influence the results since the relation between Ca, Mg, K, Si and P are important

Aluminium

Scarcely studied as an additive.

Bauxite, ore consisting of Al-oxide/hydroxide

- Investigated during combustion of waste => Potential for biomass combustion

- It was concluded that bauxite was less efficient than the clay kaolin
- Suggested reaction:

$$Al_2O_3\ (s) + 2NaCl\ (g) + H_2O\ (g) \rightarrow 2NaAlO_2 + 2HCl\ (g)$$

Aluminium-silicate

Commonly used as an additive to reduce slagging & bed agglomeration

- Bentonite
- Kaolin, clay mainly consisting of the mineral kaolinite $Al_2Si_2O_5(OH)_4$

Fine particles may be reduced by capturing of K into the Al-silicate

- Heating => kaolinite loose water and forms meta-kaolinite which has a large surface area
- Overall reactions:

$$Al_2Si_2O_5(OH)_4 + 2KCl \rightarrow 2KAlSiO_4 + H_2O + 2HCl$$

$$Al_2Si_2O_5(OH)_4 + 2KCl + 2SiO_2 \rightarrow 2KAlSi_2O_6 + H_2O + 2HCl$$

Kalsilite

Leucite

High melting K-Al-silicate minerals formed

3. Case study:

”Combustion of straw pellets with kaolin as additive”

Case study
- Combustion of straw pellets with kaolin as additive

Aim

- Investigate the possibilities to reduce the particle emission from combustion of straw pellets by supplying kaolin as additive.

Measurement plan

Comparing combustion without additive & cases using additive

1) Combustion of straw pellets

2) Straw pellets and 3 % kaolin

3) Straw pellets and 6 % kaolin

Experimental: Fuel and additive

Fuel: Straw pellets
Additive: Kaolin

	Straw	Straw/3 % kaolin	Straw/6 % kaolin
Moisture	12.7	12.3	11.9
H(lower) (MJ/kg)	17.05	16.5	15.9
C	46.9	[illegible]	[illegible]
O	42.2	[illegible]	[illegible]
H	5.9	5.7	5.5
N	0.40	0.39	0.37
S	0.07	0.07	0.07
Cl	0.13	0.13	0.12
Ash	4.4	7.7	11.0
Si	1.17	1.9	2.6
K	0.49	0.5	0.5
Ca	0.31	0.30	0.29
Mg	0.06	0.06	0.06
P	0.04	0.04	0.04
Al !	0.02	0.74	1.46
Fe	0.02	0.02	0.02
Na	0.01	0.01	0.01

Additive was mixed with the fuel prior combustion.

Experimental –Combustion equipment

Multi-stoker
Max output: 65 kW

Sonnys Maskiner AB

Boiler
Max output: 95 kW

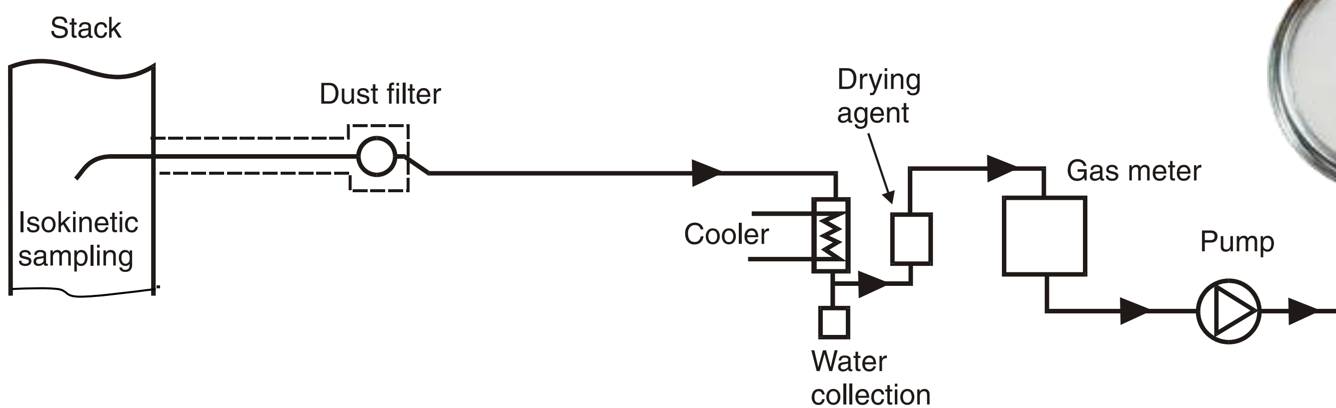
Centrometal

The multi-stoker was continously operated and the thermal output from the boiler was 29 kW.

Presented at Central European Biomass Conference, 26-29 January 2011, Graz, Austria

Experimental –Measurement methods

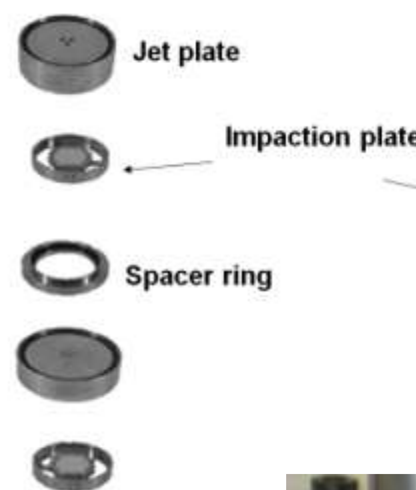
Mass concentration of particles: filter sampling

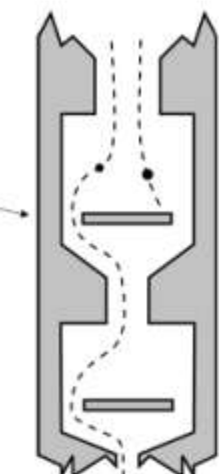


Mass size distribution

- Dekati Low Pressure Impactor (LPI), 0.030 to 10 µm (13 size classes). Substrates: polycarbonate foils

- Wet-chemical analysis of metals using ICP-OES, and of Cl and S using IC.

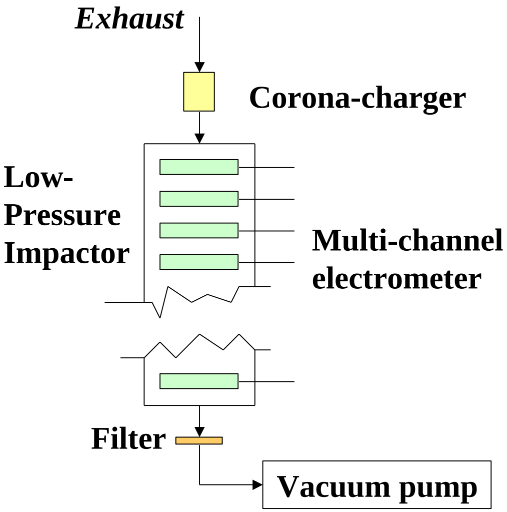




Experimental –Measurement methods

Particle number concentration and size distribution

- Electrical low pressure impactor (ELPI), 7 nm - 8 µm (13 size classes).
- Prior to ELPI-measurement, the flue gas was diluted, with dry and particle-free air, in two steps.



Gaseous compounds: oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), and OGC (organic gaseous carbon) were continuously measured to control the combustion conditions

Results

27% reduction!

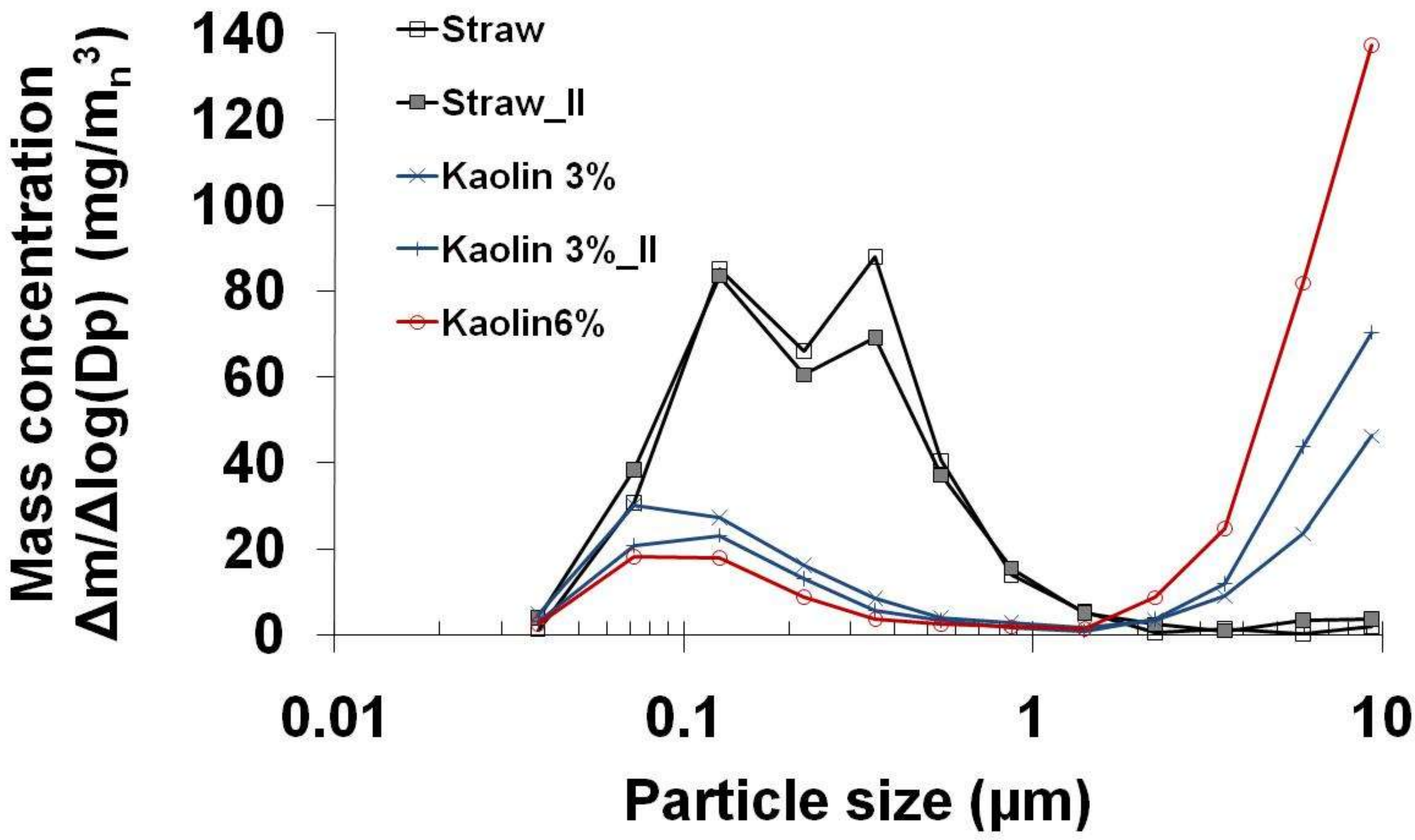
Emissions

	O_2 (%)	CO_2 (%)	CO (mg/MJ)	OGC (mg/MJ)	PM (mg/MJ)	PM (10^{12} 1/MJ)
Straw	10.9	9.3	91	3	64	14
Kaolin3%	10.4	9.7	160	3	47	26
Kaolin6%	10.7	9.1	230	4	73	24

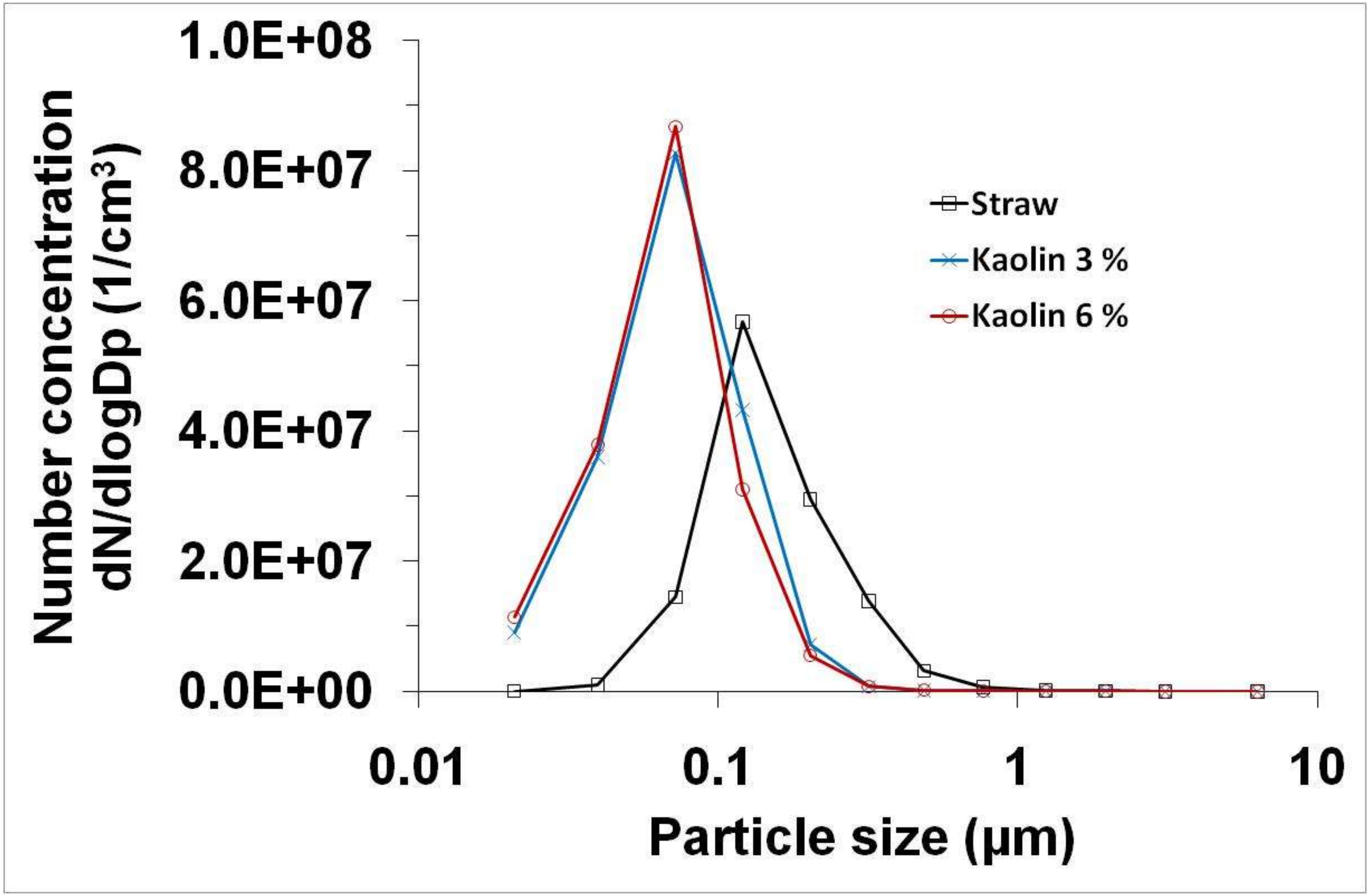
14% increase?!

- Combustion of straw pellets (Reference) – Comprehensive slagging
- Addition of kaolin => No slagging problems

Mass size distributions

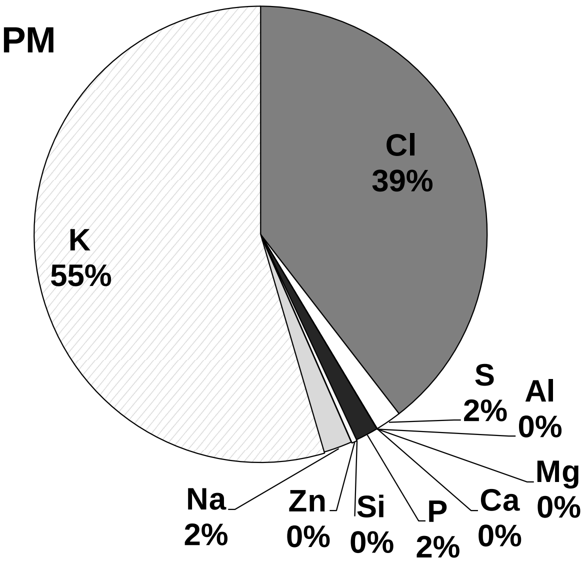


Number size distributions



Chemical composition of the particles

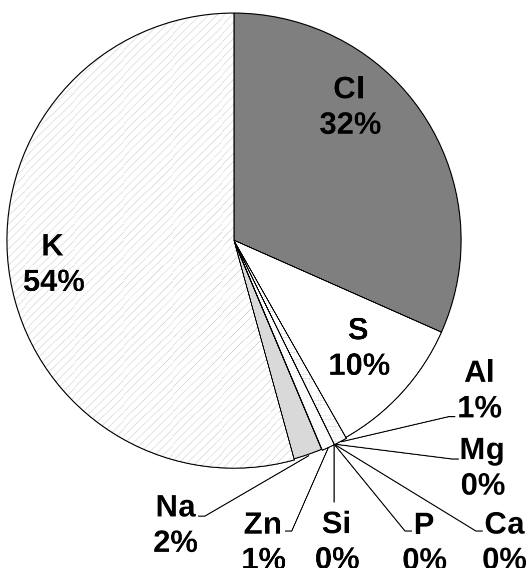
Ref: Fine PM



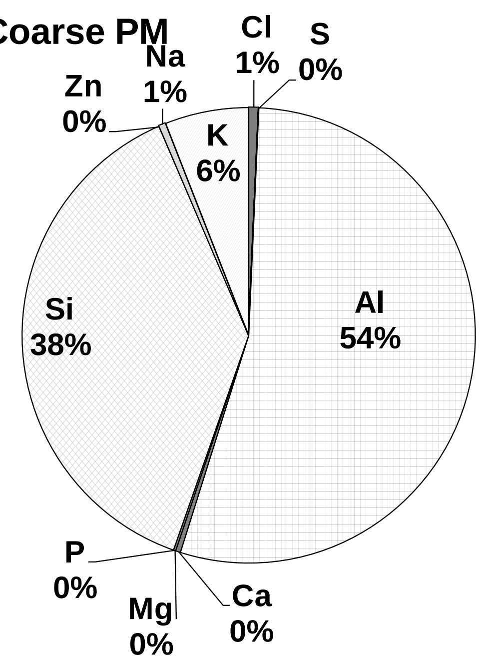
Ref: Coarse PM:

Under detection limits.

Kao6: Fine PM



Kao6: Coarse PM



Conclusions of the case study

- Not recommended to fire straw pellets in the stoker investigated because of slagging. A possible solution to the problem is to use kaolin as an additive to the fuel.

Summary

1. **Additives for minimisation of emissions of fine particles**

   Overall mechanism: Capturing gaseous K into high-temperature melting compounds.

   Main groups depending of chemical composition:

   - **Calcium**: Shown for P-rich fuels. High-melting compounds = Ca-K-Phosphates
   - **Phosphorus:** High-melting compounds = Ca-K-Phosphates
   - **Aluminium:** Shown for waste. High-melting compounds = Alkali-Al-Oxides
   - **Aluminium-silicate**: High-melting compounds = K-Al-Silicates

Thank you!