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Characterisation methods for solid biomass fuels regarding their thermal utilisation in fixed-bed reactors

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Introduction

- **Main biomass groups: woody biomass, herbaceous biomass, fruit biomass (agricultural residues), and blends and mixtures**
  - Different physical behaviour and **chemical compositions** typical **for different biomass groups**
  - Higher amounts of ash, N and ash forming elements (e.g. S, Cl, Si, K, P) for herbaceous biomass compared to woody biomass
- **Increased utilisation of alternative biomass feedstocks (herbaceous biomass and agricultural residues) for combustion purposes can cause:**
  - Ash-related problems (ash melting on grates, deposit formation and corrosion)
  - Increased particulate, NO_x, SO_x and HCl emissions
- **One strategy to minimise problematic combustion behaviours is the application of fuel additives and fuel blends**
- **Up to now the evaluation of mixing ratios of fuel additives and fuel blends is mainly based on experiences and trial and error methods**

Objectives

- **Development of characterisation methods in order to minimise the necessity for time-consuming and expensive real-scale combustion tests**
- **Development of characterisation methods/tools for solid biomass to predict combustion-related properties based on laboratory approaches and appropriate calculation procedures; focusing on fixed-bed combustion**
  - Targeted selection of biomass mixtures and biomass additives to improve the combustion behaviour by **fuel indices, thermodynamic equilibrium calculations** (TEC) and **fixed-bed lab-scale reactor experiments**
- **Development of a new single particle reactor**
  - Determine relevant parameters during the thermal conversion process → simultaneously record **time resolved release profiles of relevant inorganic aerosol forming elements** (S, Cl, K, Na, Zn and Pb)

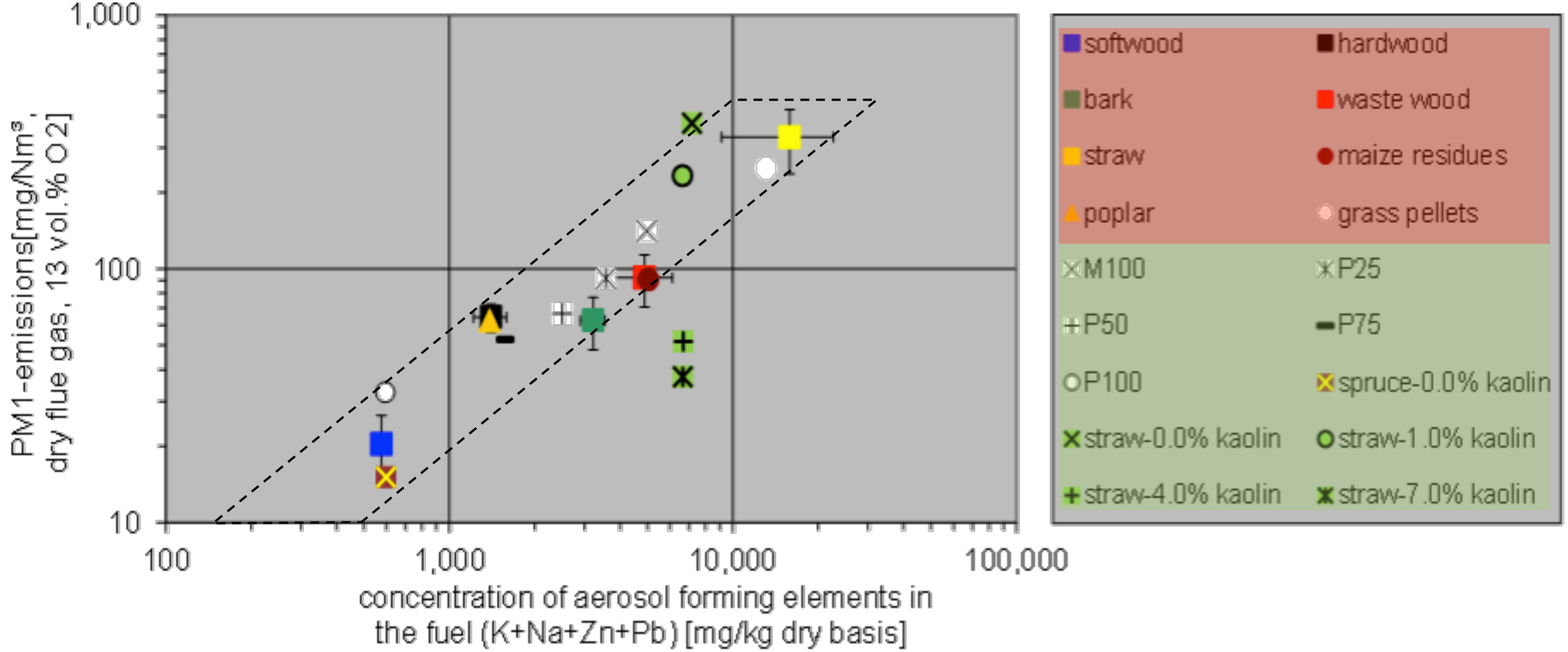
Fuel indices – Methodology

- **Fuel and ash analysis**
  - Only **highly accurate analytical methods** applied
  - Fuel sample has to be **representative** for the fuel of interest → different parts (e.g. leaves, stalks, grains, fruit) of a plant may show strongly deviating chemical compositions
- **Plenty of coal indices available → not applicable for biomass fuels**
- **Fuel indices can be used for a qualitative pre-evaluation of combustion related problems**
- **Fuel indices are based on results of chemical analyses, theoretical considerations, experiences from lab,- pilot- and real-scale combustion tests**
- **Relevant fuel properties are correlated with**
  - Gaseous and **particulate** emissions
  - Release ratios of relevant inorganic aerosol forming elements
  - Ash melting temperature
  - Corrosion risks
- **Validated by results of grate furnace combustion tests in the power range between 140 kW_{th} and 110 MW_{th}**

Fuel indices – Overview

- **Fuel indices that have been investigated/defined:**
  - N-concentration in the fuel as an indicator for NO_x emissions
  - **Sum of K, Na, Zn and Pb** as an indicator regarding **aerosol emissions** and deposit build-up
  - Molar Si/K ratio for an estimation of the K release from the fuel to the gas phase
  - Molar 2S/Cl ratio as an indicator for high-temperature corrosion risks
  - Molar (K+Na)/[x·(2S+Cl)] ratio to predict the gaseous SO_x and HCl emission range to be expected
  - The prediction of the ash melting temperatures with the molar Si/(Ca+Mg), the molar (Si+K+P)/(Ca+Mg) ratio as well as the molar (Si+K+P)/(Ca+Mg+Al) ratio

Fuel indices – Example: Aerosol emissions



Explanations: PM1... particles smaller 1 µm (aerosols);

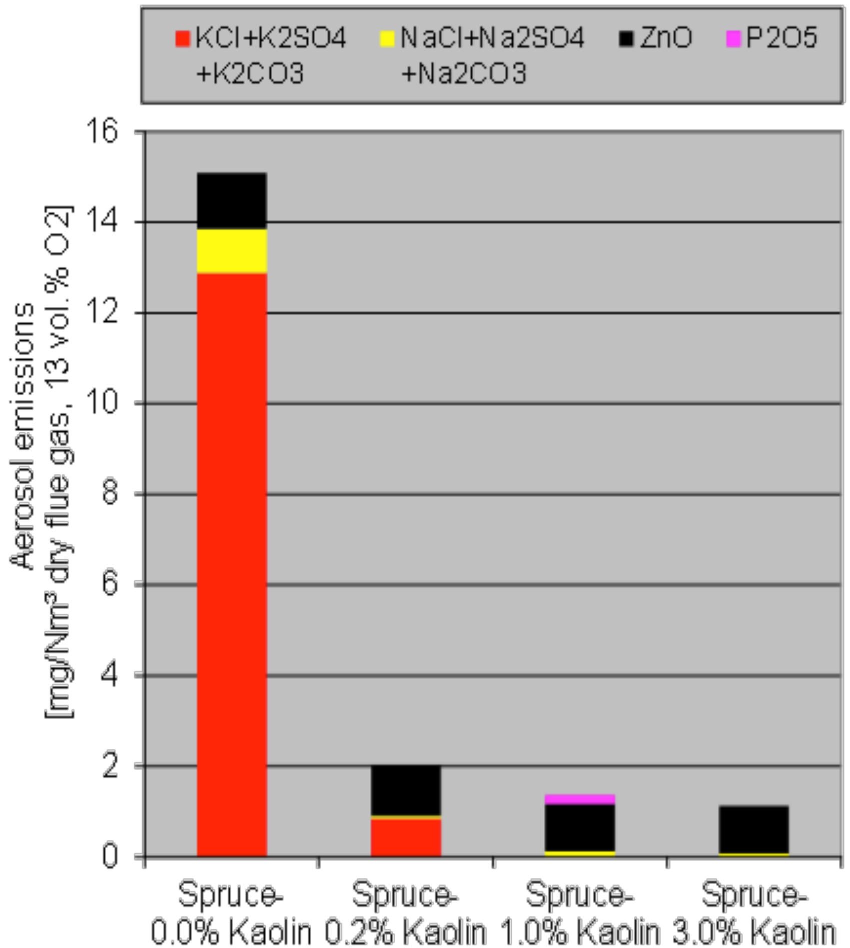
data origin: full-scale combustion tests; fixed-bed lab-scale reactor tests

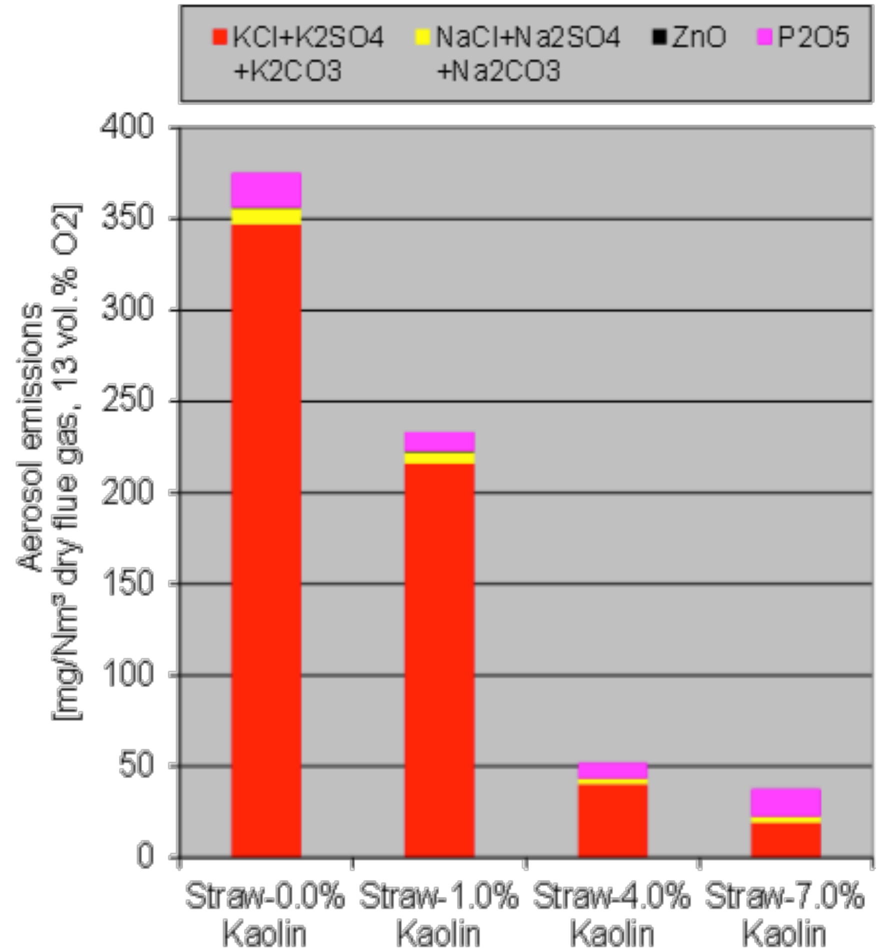
- **With increasing concentration of K, Na, Zn and Pb in the fuel the aerosol emissions rises**
- **Index applicable for fuel blends, not valid for biomass/kaolin mixtures**

Fixed-bed lab-scale reactor – Description

- **Batch type reactor to simulate the fuel decomposition behaviour in real-scale grate combustion systems**
- **Tests with the lab-scale reactor provide results on:**
  - Combustion behaviour
  - Release of NO_x precursors
  - **Release of aerosol forming elements** from the fuel to the gas phase
  - First indications about the ash melting tendency (optical evaluation)

Fixed-bed lab-scale reactor – Example: Prediction of aerosol emissions





Predicted aerosol emissions (by fixed-bed lab-scale reactor experiments) for pure spruce and spruce/kaolin mixtures as well as for straw and straw/kaolin mixtures

Thermodynamic equilibrium calculations – Description

- **Thermodynamic equilibrium calculations (TEC) provide information regarding:**
  - Ash composition and fractionation of individual elements in solid, liquid and gaseous phases
  - Composition of phases formed
  - **Release of relevant aerosol forming elements** (S, Cl, K, Na, Zn, Pb)
  - Ash melting behaviour

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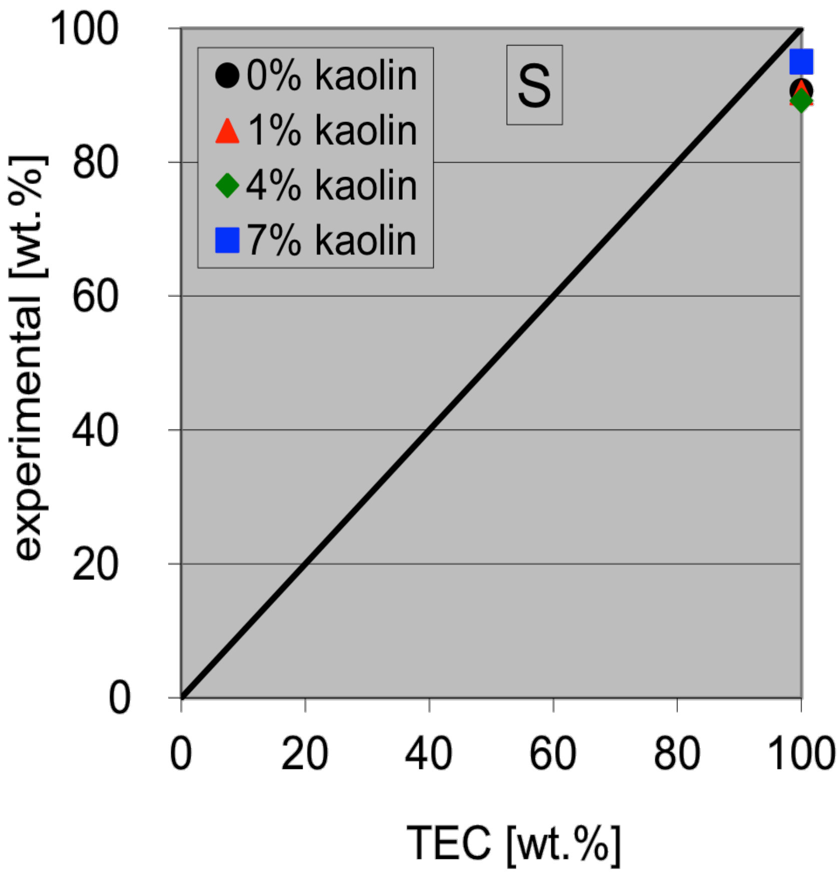
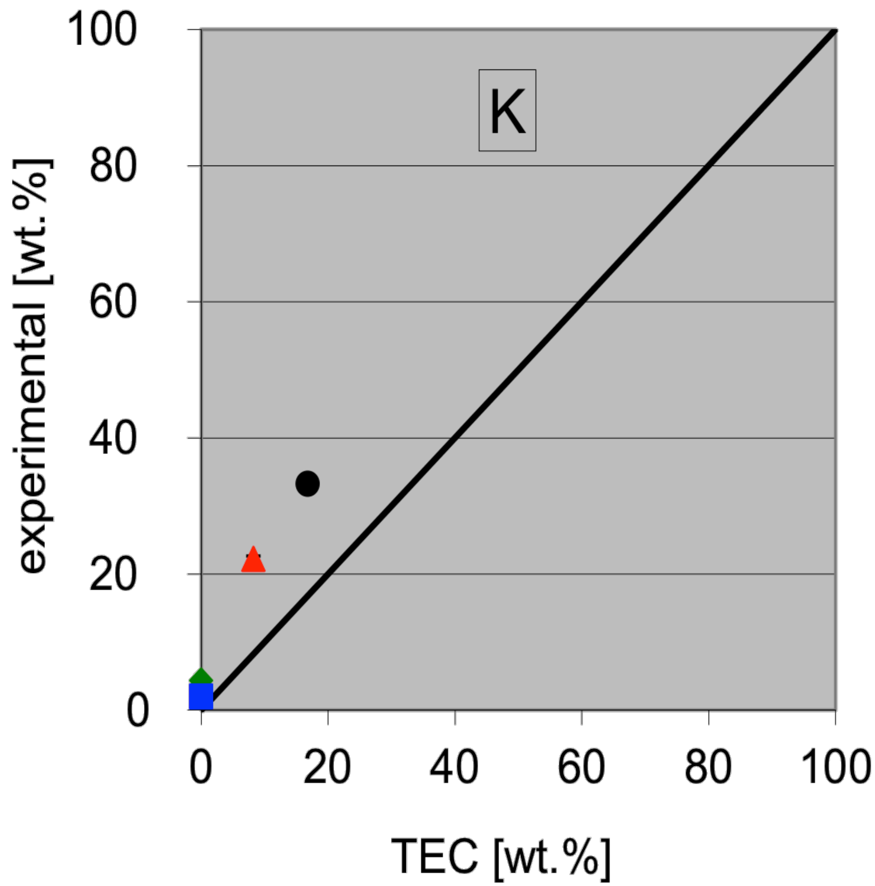
Thermodynamic equilibrium calculations – Example: Release of S and K





Experimentally determined element release of S and K by fixed-bed lab-scale reactor experiments in comparison with TEC for pure straw and straw/kaolin mixtures

<u>Explanation:</u> TEC .. thermodynamic equilibrium calculations

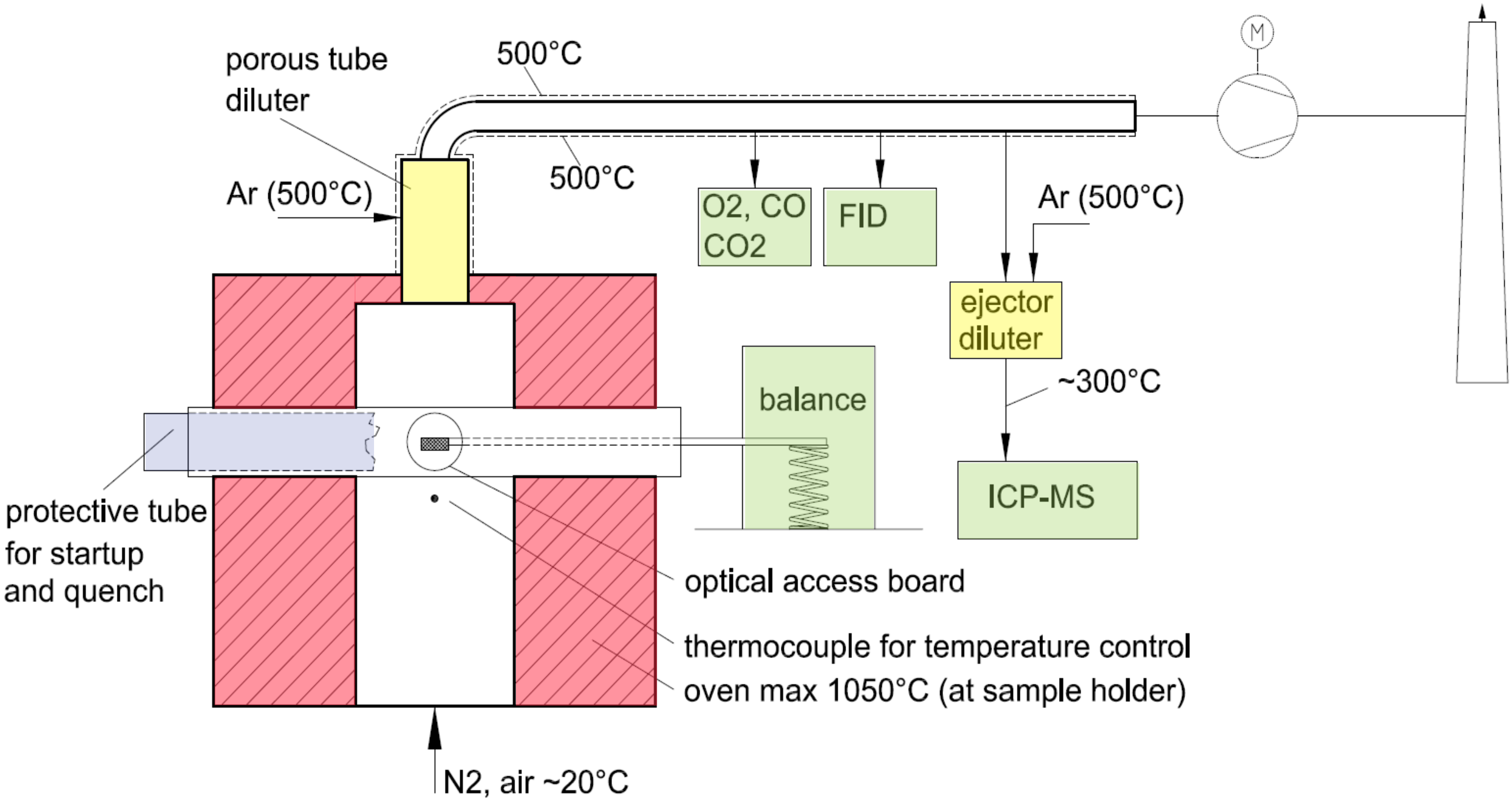
Single particle reactor – Background & objectives

- **Release of inorganic components during biomass combustion/ gasification → special relevance:**
  - Aerosol formation, deposit build-up and boiler tube corrosion
- **Most studies describe the release during batch or real-scale experiments**
  - Integral release rate (entire combustion experiment)
- **Objectives of the single particle reactor development**
  - Development of a **single particle reactor** that enables a **characterisation** of the **combustion process** as well as an **online determination** of **volatile ash forming elements** released, by connecting the reactor to an inductively coupled plasma mass spectrometer (ICP-MS)

Single particle reactor – Methodology

- **Reactor concept is based on a macro thermogravimetric analyser (TGA)**
  - Online recording of weight loss, temperatures
- **Batch type single particle reactor (SPR)**
- **2-step dilution of the sample gas**
  - **Porous tube diluter** → needed regarding the detection limits of the gas analyser
  - **Ejector diluter** → diluted gas flow to the ICP-MS
- **Online measurement of relevant aerosol forming elements:**
  - ICP-MS: Agilant Technologies series 7700x
    - Recorded intensities: ^{13}C, ^{34}S, ^{23}Na, ^{35}Cl, ^{39}K, ^{66}Zn, ^{132}Xe, ^{208}Pb
- **Quantification of the recorded intensities over the integral release rate**
  - Element balance for fuel and ash residues

Single particle reactor – Complete setting



<u>Explanation:</u> FID … flame ionisation detector, ICP-MS … inductively coupled plasma spectrometer

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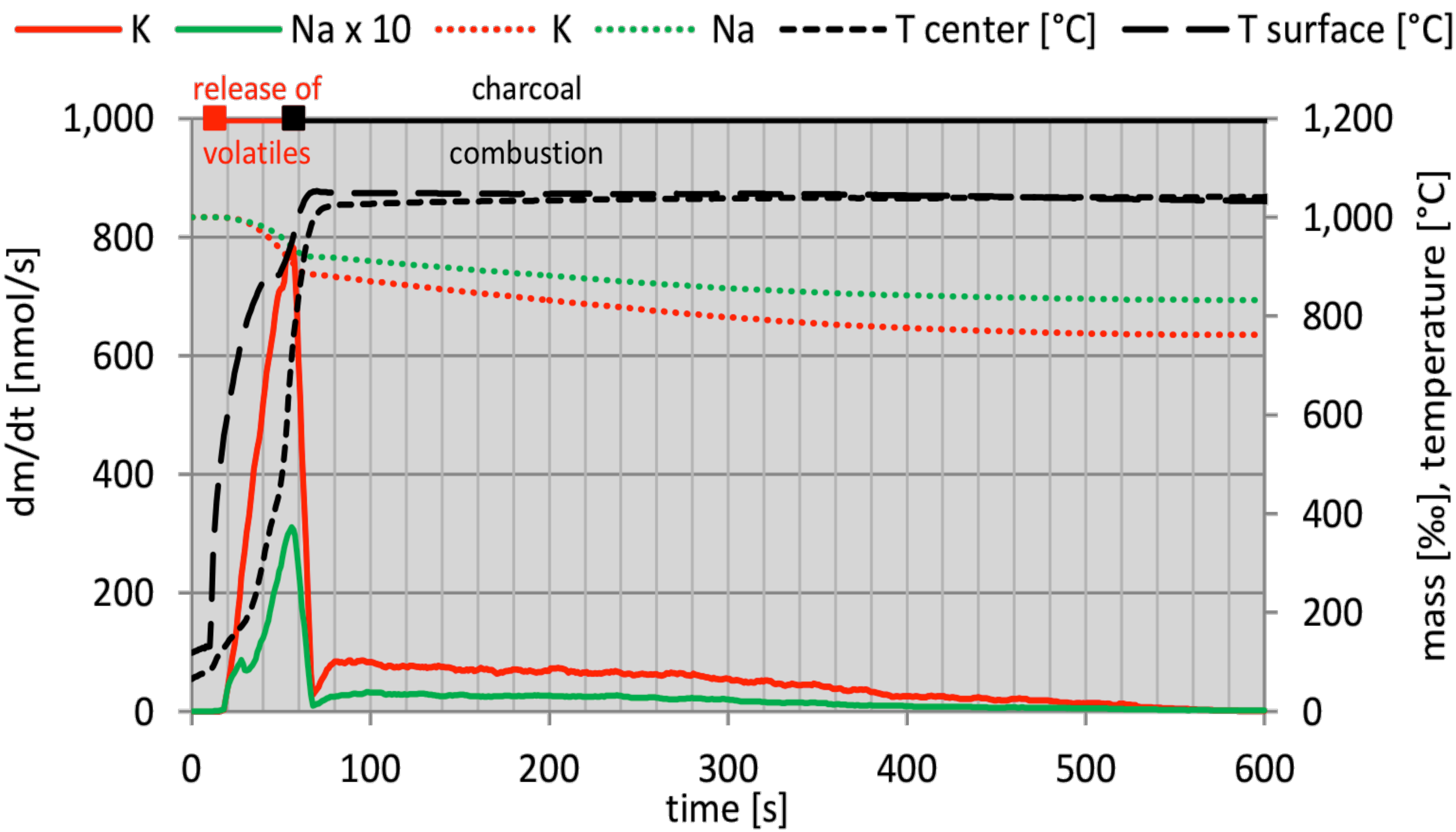
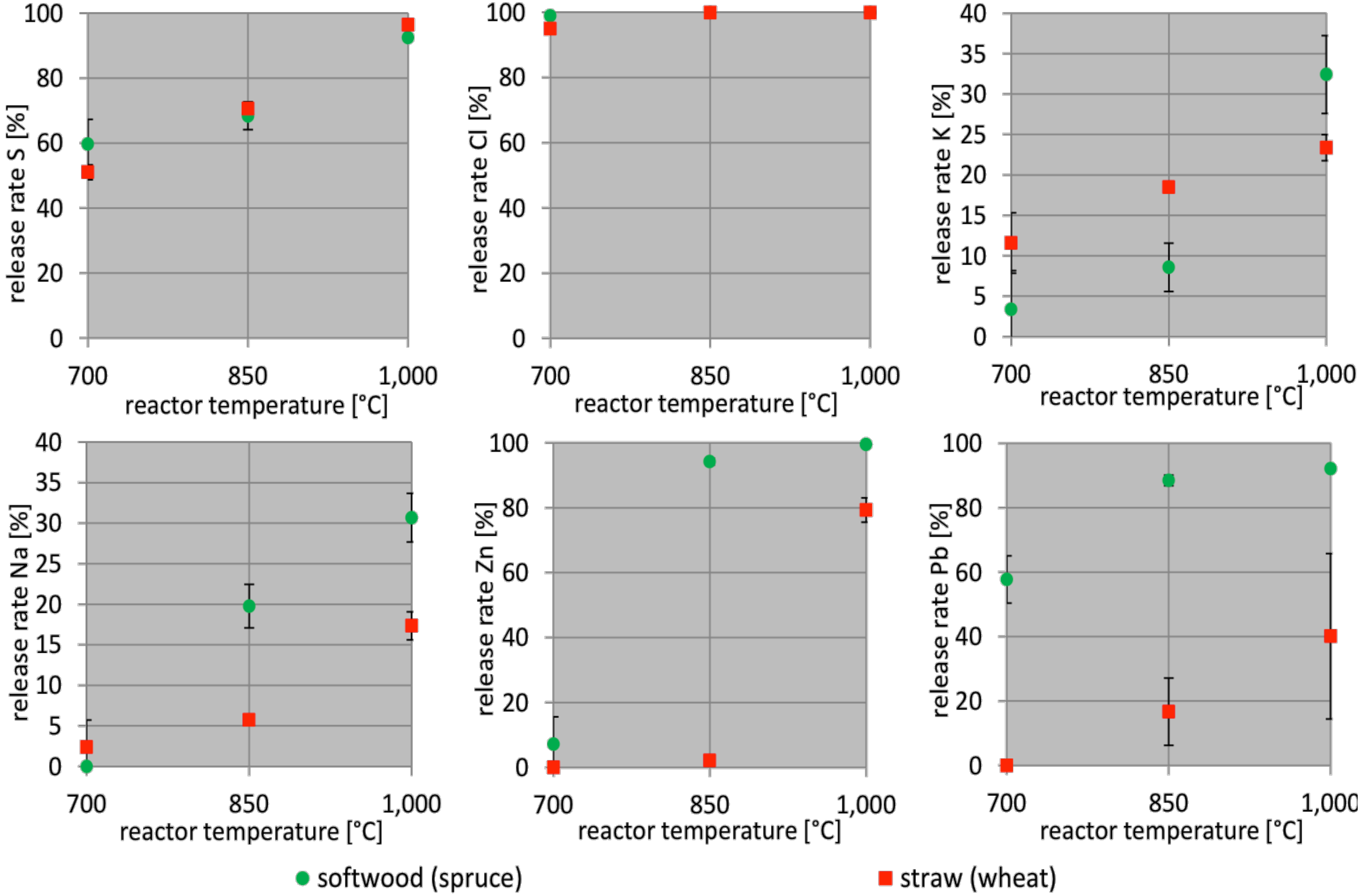
Single particle reactor – Example: Time resolved release behaviour of K and Na



Time dependent release of K and Na from straw at reactor temperatures of 1,000°C

Single particle reactor – Example: Release rates for softwood and straw at 6 vol.% O_2



Explanation: Release rates related to the element content in the biomass fuels

Summary and conclusions

- **Fuel indices can be used for a pre-evaluation regarding the combustion behaviour**
- **TEC can be applied for a qualitative determination of the release of aerosol forming elements and the ash melting behaviour**
- **For a quantitative evaluation of the release of aerosol forming elements fixed-bed lab-scale reactor tests can be performed**
- **For inorganic element release in dependence of time and particle-temperature a new single particle reactor is available**
  - More detailed insight into release behaviour and release processes possible
- **This is a general approach for a comprehensive fuel characterisation also applicable for biomass additive mixtures and fuel blends**
  - By these methods the need for **cost and time intensive full-scale combustion tests** can be **minimised**

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Thank you for your attention!

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