Advanced biomass fuel characterisation methods

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Introduction and objectives (I)

- To widen the available biomass feedstock potential for heat and power production
  - agricultural biomass
  - biogenic residues
  - energy crops

  gain rising interest on the fuel market.

- These feedstocks are typically so-called difficult fuels in terms of combustion related issues. Compared with conventional chemically untreated wood fuels they usually contain increased
  - contents of ash forming elements (especially Si and K)
    ➔ higher risks for slagging, deposit formation and particulate emissions
  - S, Cl and N contents
    ➔ higher gaseous emissions (SO_x, HCl, NO_x)
    ➔ elevated high temperature Cl corrosion risks

Introduction and objectives (II)

- **Different approaches have been developed to improve the combustion behaviour of difficult biomass fuels**
  - **leaching**
  - **torrefication**
  - **fuel blending and additive utilisation**

- **Especially regarding ash related problems the utilisation of inorganic additives provides the possibility to create designer fuels with significantly improved combustion properties from problematic feedstocks.**

- **Advanced fuel characterisation methods can provide an important basis for**
  - **the combustion related characterisation of difficult biomass fuels for which no long-term experience concerning their combustion properties is available**
  - **to quickly evaluate fuel blends and fuel-additive-mixtures in order to asses problematic combustion related issues.**

- **For that purpose a 3-step evaluation procedure has been developed**

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Assessment of biomass fuels, blends and fuel/additive mixtures – 3-step procedure

STEP 1

Combustion related characterisation of

- the original fuel
- blends resp. mixtures of the fuel with potential additives

by

- **chemical analyses**
- **evaluation of fuel indexes**

- **Gain first estimates on ash related properties and how they can be influenced by blending and additivation**
- **Identification of meaningful additives and reasonable additive/fuel mixing rates**

- **Qualitative information**

STEP 2

Thermodynamic high temperature equilibrium calculations for

- fuels
- mixtures of the fuel with potential additives

Improved understanding regarding difficult fuels and the influence of blending and selected additives on

- **ash transformation**
- **ash melting**
- **element release**

- **Semi-quantitative information**

STEP 3

Lab-scale reactor combustion tests with

- selected fuel/additive mixtures

- **Information regarding the combustion process**
- **Release data for N species as well as inorganic compounds (K, Na, S, Cl)**
- **Indications regarding the ash melting behaviour**

- **Quantitative information**

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Methodology – Step 1: chemical analyses and evaluation of fuel indexes (I)

➢ Fuel sampling

- **Agricultural biomasses, biogenic residues and energy crops usually show a wide range of compositions**
- **Therefore, representative fuel sampling is a relevant initial issue**

➢ Fuel analyses

- **Only highly accurate methods specially developed for biomass fuels shall be used**
- **It is recommended to analyse the original fuel and not ashed fuel samples**
- **Proposed analyses methods for the determination of the contents of major ash forming elements**
  - in accordance with EN 15290 (part A) the fuel is digested in a closed vessel by the help of reagents, temperature and pressure
  - proposed mixture of reagents: HNO_3 (65%) / HF (40%) / H_3BO_3

Methodology – Step 1: chemical analyses and evaluation of fuel indexes (II)

➢ Evaluation of fuel indexes

- **Fuel indexes are defined in order to provide first indications regarding relevant combustion related properties of biomass fuels**
  (e.g. gaseous NO_x, SO_x and HCl emissions, ash related problems)
- **Fuel indexes are based on the physical behaviour, chemical reaction pathways as well as interactions between certain elements during combustion.**
- **Specific fuel indexes, tailored to biomass fuels as well as fixed-bed combustion, have been developed and their applicability has been proven.**
- **Within the fuel characterisation strategy introduced the following fuel indexes are of major relevance:**
  - molar Cl/Si ratio → K release (aerosol formation)
  - molar (Si+P+K)/(Ca+Mg+Al) ratio → ash melting behaviour
  - molar (K+Na)/[x(2S+Cl)] ratio → HCl and SO_x formation
  - molar 2S/Cl ratio → high temperature Cl-corrosion

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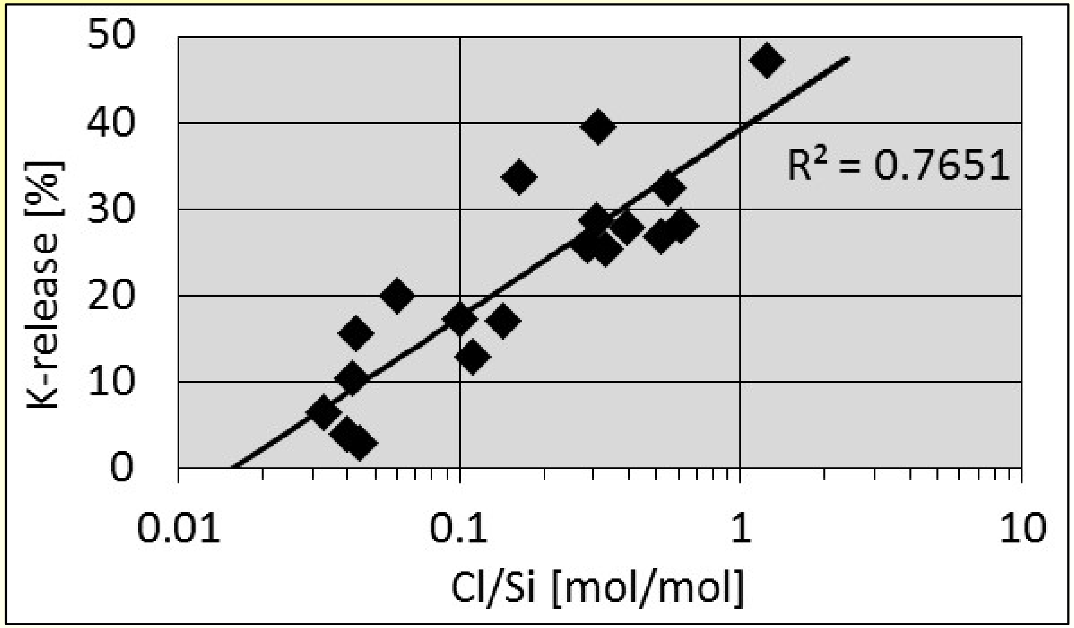
Methodology – Step 1: chemical analyses and evaluation of fuel indexes (III)

molar Cl/Si ratio



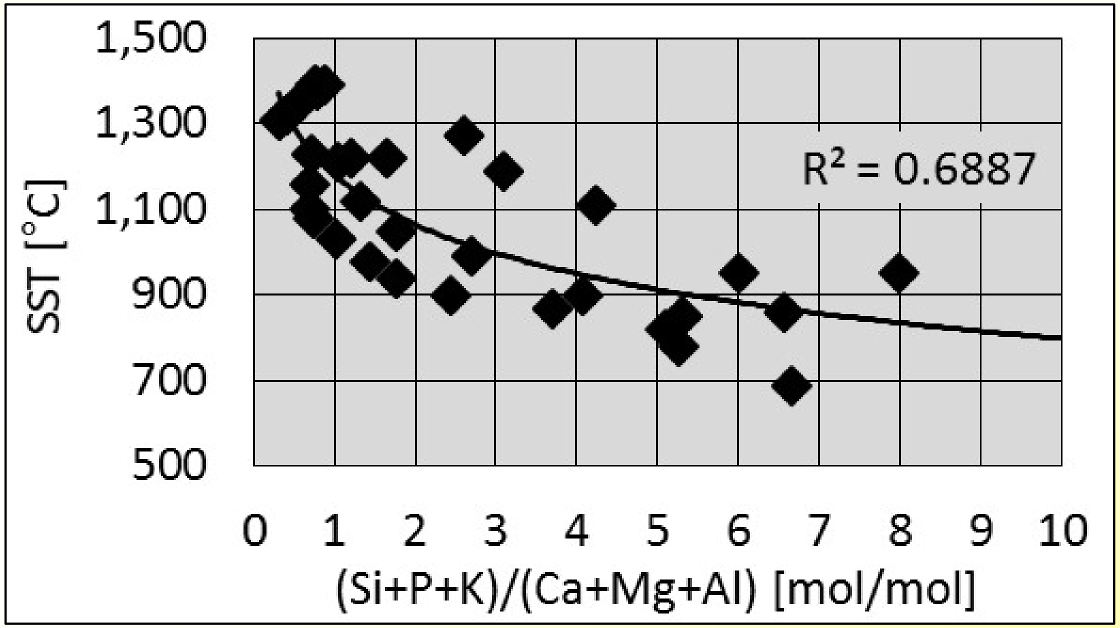
Release in wt% of the K in the fuel

The correlation is statistically significant

Data taken from pilot and real scale test runs at grate-fired boilers performed by BIOS BIOENERGIESYSTEME GmbH

- **Increasing K-release with increasing value of the index**

molar (Si+P+K)/(Ca+Mg+Al) ratio



SST … shrinkage starting temperature

The correlation is statistically significant

Data taken from the internal biomass fuel database of BIOS BIOENERGIESYSTEME GmbH

- **Decreasing ash melting temperatures with increasing value of the index**

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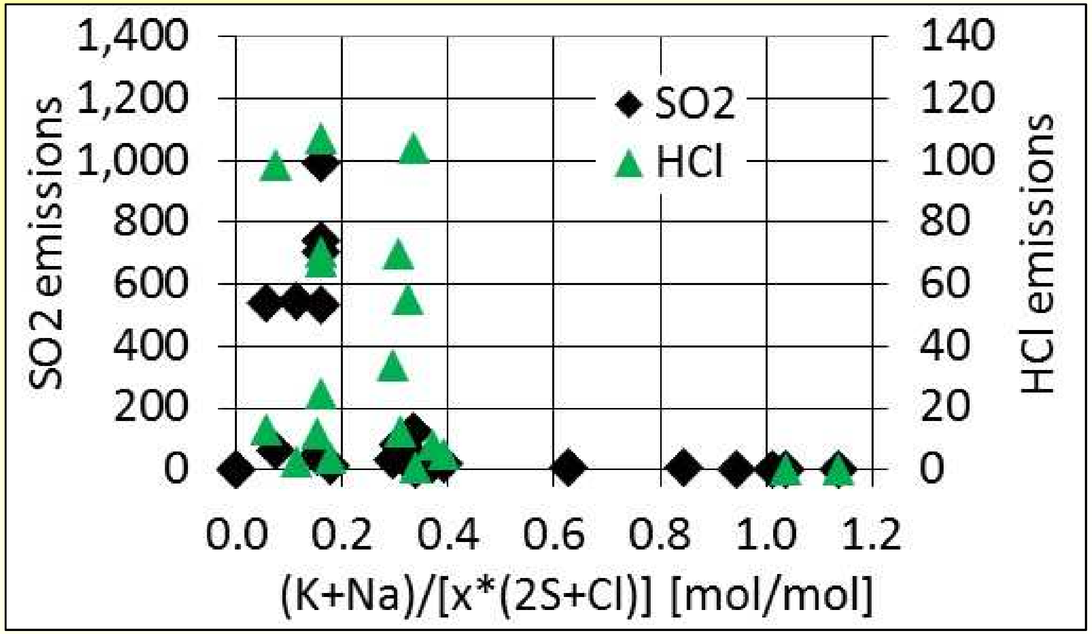
Methodology – Step 1: chemical analyses and evaluation of fuel indexes (IV)

molar (K+Na)/(x(2S+Cl)] ratio



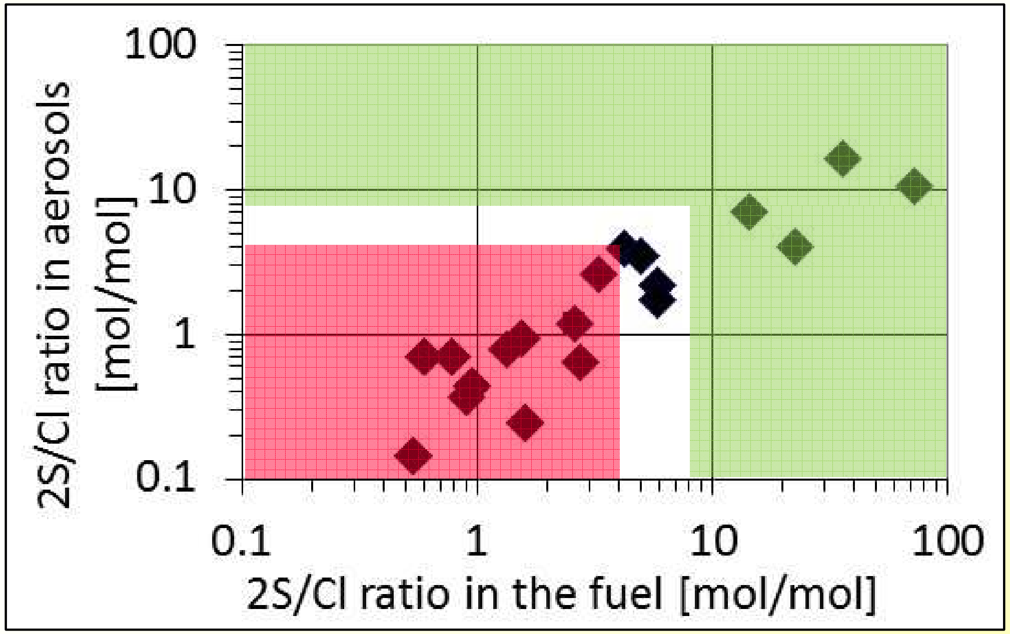
emissions in mg/Nm³ related to dry flue gas and 13 vol% O_2

Data taken from pilot and real scale test runs at grate-fired boilers performed by BIOS BIOENERGIESYSTEME GmbH

x typically between 2 and 15

- **Index values <0.4 indicate increasing SO_2 and HCl emissions**

molar 2S/Cl ratio



Data taken from the internal biomass fuel database of BIOS BIOENERGIESYSTEME GmbH

- **2S/Cl < 4: high high temperature corrosion risk**
- **2S/Cl > 8: low high temperature corrosion risk**

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Methodology – Step 2: thermodynamic high temperature equilibrium calculations (TEC)

- **TEC provide the possibility to investigate the**
  - **release behaviour of inorganic compounds**
  - **ash melting behaviour**
- **TEC are performed under the assumption that chemical equilibrium can be reached for the system investigated**
- **Applied software and databases**
  - **FactSage 6.2**
  - **component database Fact 53**
  - **solution databases FToxid (slags and other oxide mixtures) and FTsalt (liquid and solid salt phases)**
- **More than 1,000 components and 9 solutions (which have been shown to be stable and thermodynamically relevant) have been considered**
- **The selection has been done application oriented for biomass fuels and ashes.**
- **Temperature range typically evaluated: 700 – 1,600°C**

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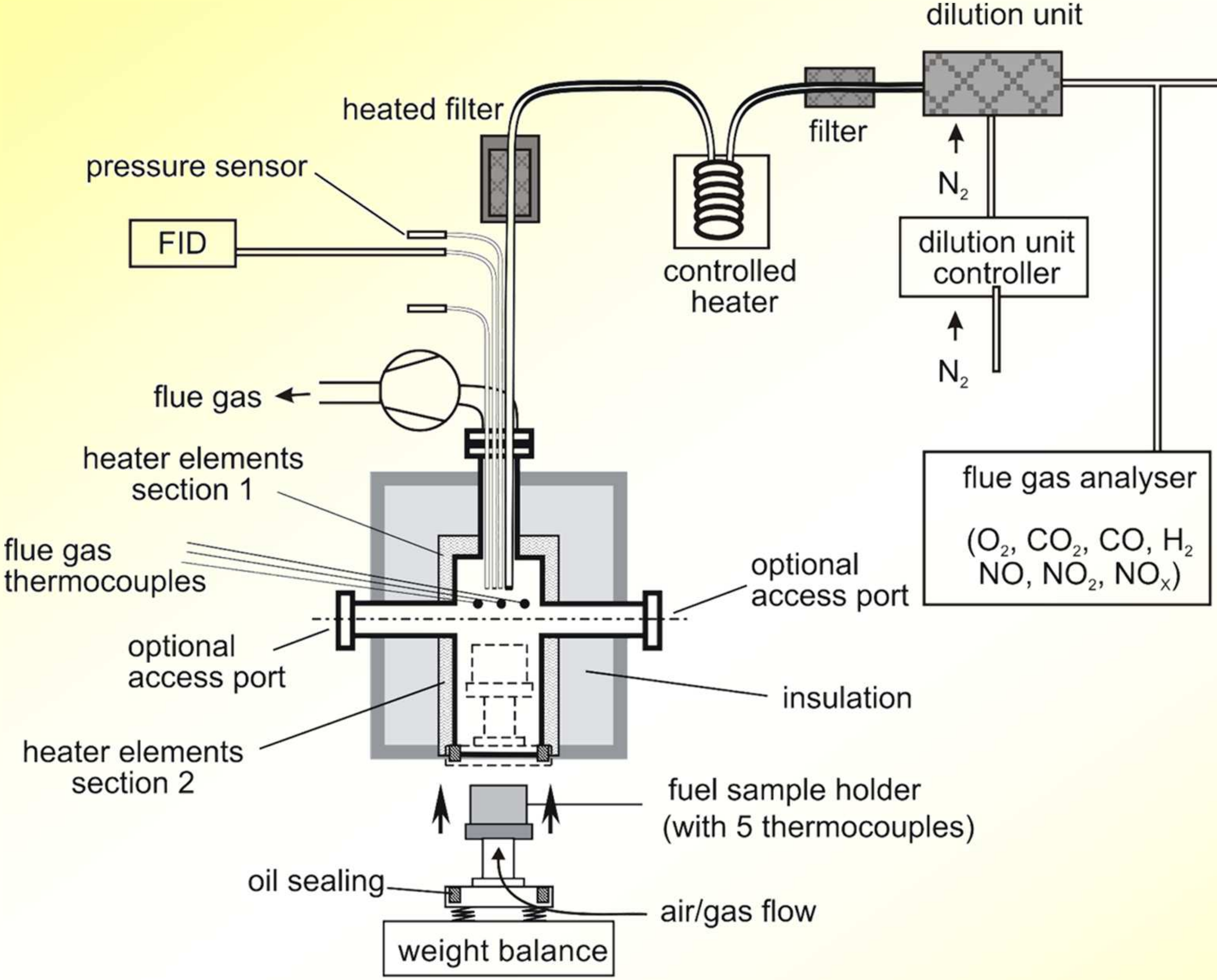
Methodology – Step 3: lab-scale reactor tests



- **Reactor temperature selectable (reactor is pre-heated)**
- **Oxidation medium selectable (passes through the fuel bed)**
- **Comprehensive flue gas analyses**
- **Analyses of the fuel and the residues (ashes)**
- **Decomposition process can be followed by thermocouples in the fuel bed**

Example: Fixed-bed lab-scale reactor of Graz University of Technology

Ref.: BRUNNER T., et al., 2013: Advanced biomass fuel characterisation based on tests with a specially designed lab-reactor. Energy Fuels, 2013, 27 (10), pp 5691–5698

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Step 1: Chemical composition and selected fuel indexes – examples: wheat and rape straw, maize residues

		maize residues	wheat straw	rape straw
ash content	wt% d.b.	2.08	6.46	7.90
S	mg/kg d.b.	475	926	3,420
Cl	mg/kg d.b.	1,870	1,730	6,790
Si	mg/kg d.b.	1,890	19,000	3,260
Ca	mg/kg d.b.	540	2,920	13,100
Mg	mg/kg d.b.	578	978	1,830
K	mg/kg d.b.	7,180	7,990	18,200
Na	mg/kg d.b.	42	84	956
P	mg/kg d.b.	774	510	650
Al	mg/kg d.b.	219	388	671
Fe	mg/kg d.b.	239	202	360
Mn	mg/kg d.b.	14	29	22
x		3.45	4.43	1.49
(K+Na)/x(2S+Cl)	mol/mol	0.65	0.44	0.84
(Si+P+K)/(Ca+Mg+Al)	mol/mol	6.08	7.04	1.41
Cl/Si	mol/mol	0.78	0.07	1.65
2S/Cl	mol/mol	0.56	1.18	1.11

Explanations: data of representative fuel samples taken during a project performed by the IPPT/ TU Graz and BIOS BIOENERGIESYSTEME GmbH (FFG-project 838762, AgroAdd-Fuels), d.b. … dry basis

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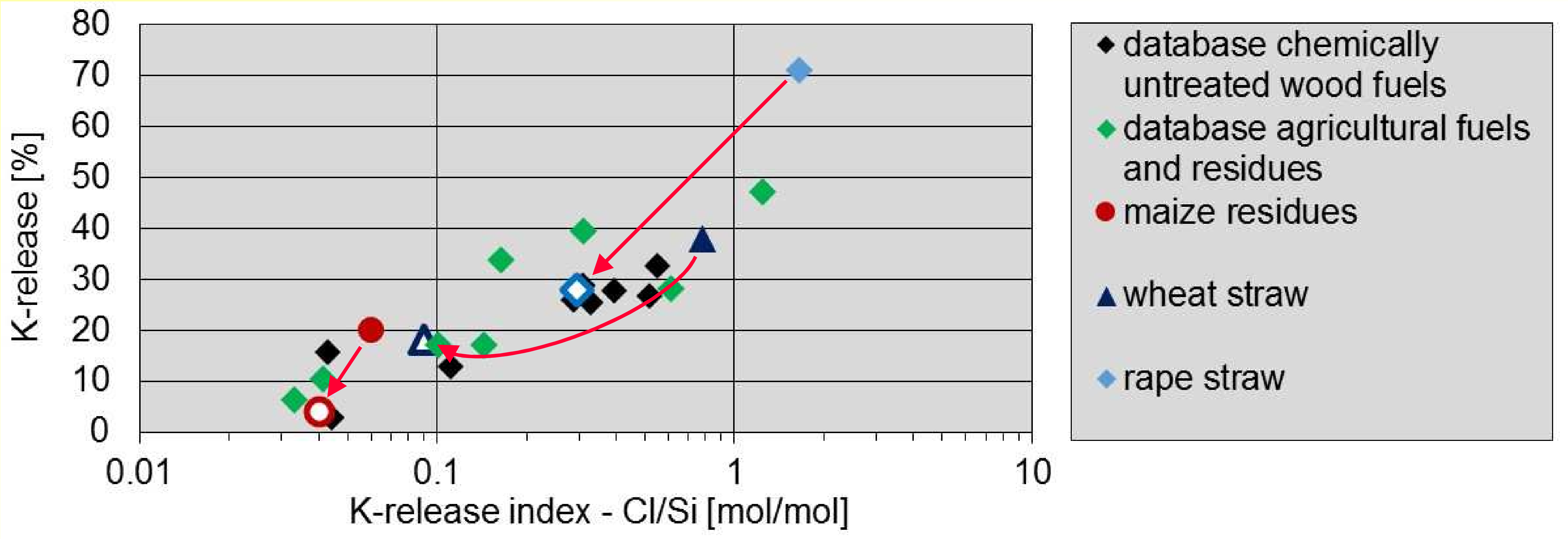
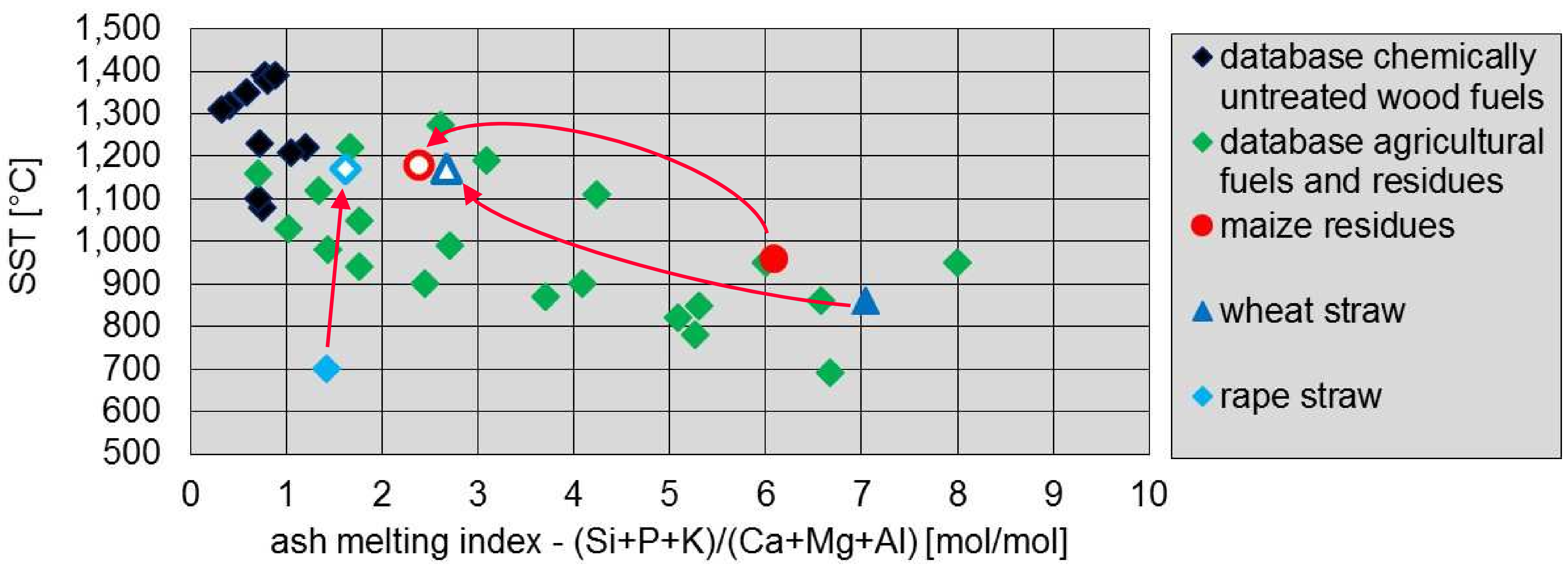
Step 1: Evaluation of selected fuel indexes (I)



Explanations: Database values from lab-scale reactor tests

wheat straw:	full symbol: pure wheat straw open symbol: wheat straw additivated with 4 wt% kaolin
rape straw:	full symbol: pure wheat straw open symbol: wheat straw additivated with 4 wt% bentonite
maize residues:	full symbol: pure wheat straw open symbol: wheat straw additivated with 6 wt% bentonite

Step 1: Evaluation of selected fuel indexes (II)



Explanations: SST: shrinkage starting temperature determined according to CEN/TS 15370-1

wheat straw: full symbol: pure wheat straw
open symbol: wheat straw additivated with 4 wt% kaolin

maize residues: full symbol: pure wheat straw
open symbol: wheat straw additivated with 6 wt% bentonite

rape straw: full symbol: pure wheat straw
open symbol: wheat straw additivated with 4 wt% bentonite

The low SST of rape straw is due to its high K content. The deformation temperature is with 900°C at the lower level of the database values for the other fuels

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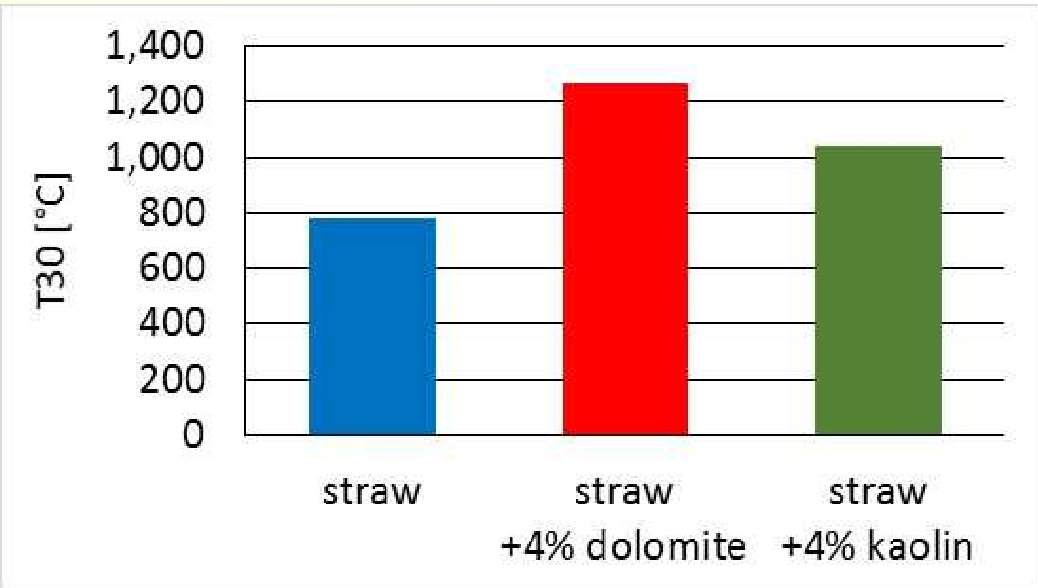
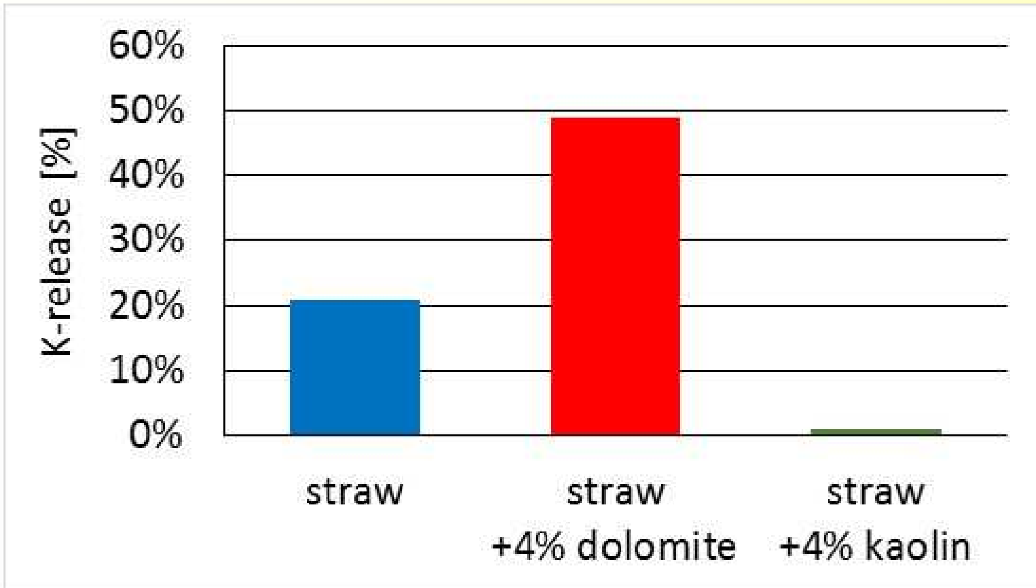
Step 2: thermodynamic high temperature equilibrium calculations (TEC) (I)

- **TEC can provide in-depth information regarding ash transformation, especially with respect to**
  - **ash melting and**
  - **K release**

  Therefore, they are especially for investigations regarding fuel blending and additive selection a valuable tool.
- **In the example below, the T30 (temperature at which 30% of the ashes according to TEC occur in molten phases) has been used as an indicator for the shrinkage starting temperature.**





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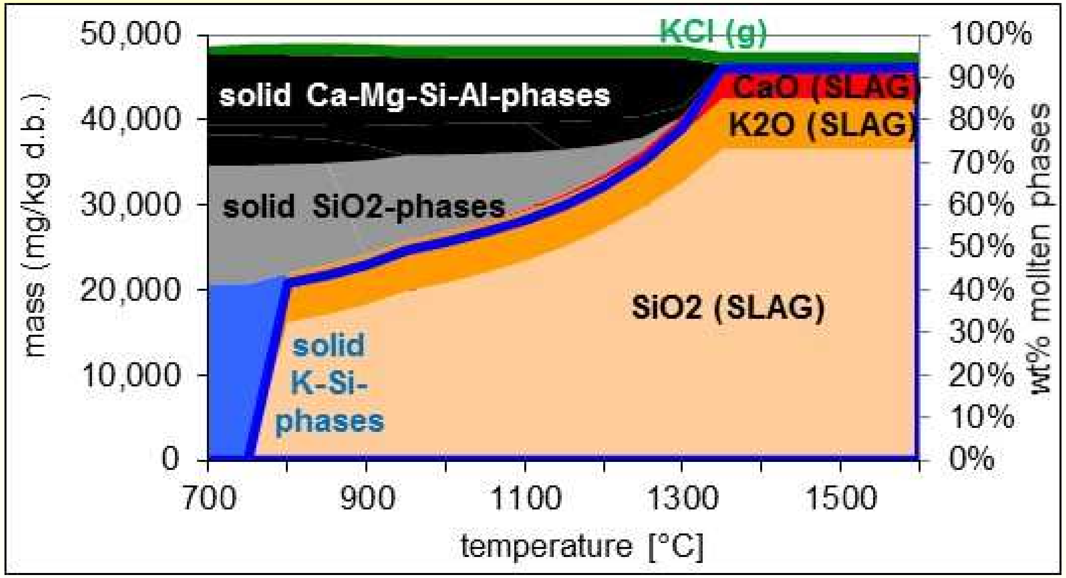
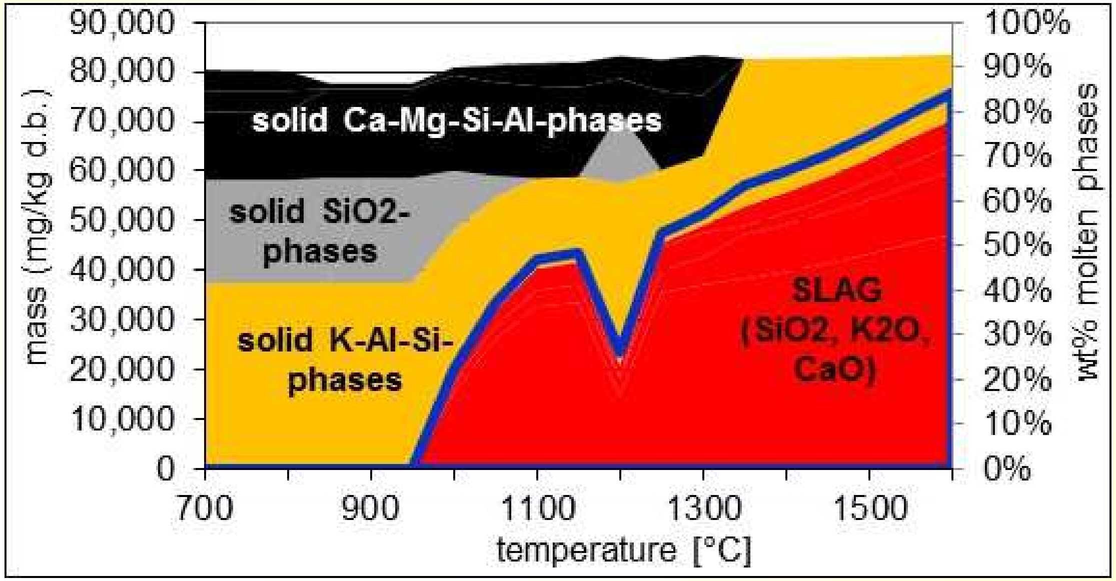
Step 2: thermodynamic high temperature equilibrium calculations (TEC) (II)

wheat straw

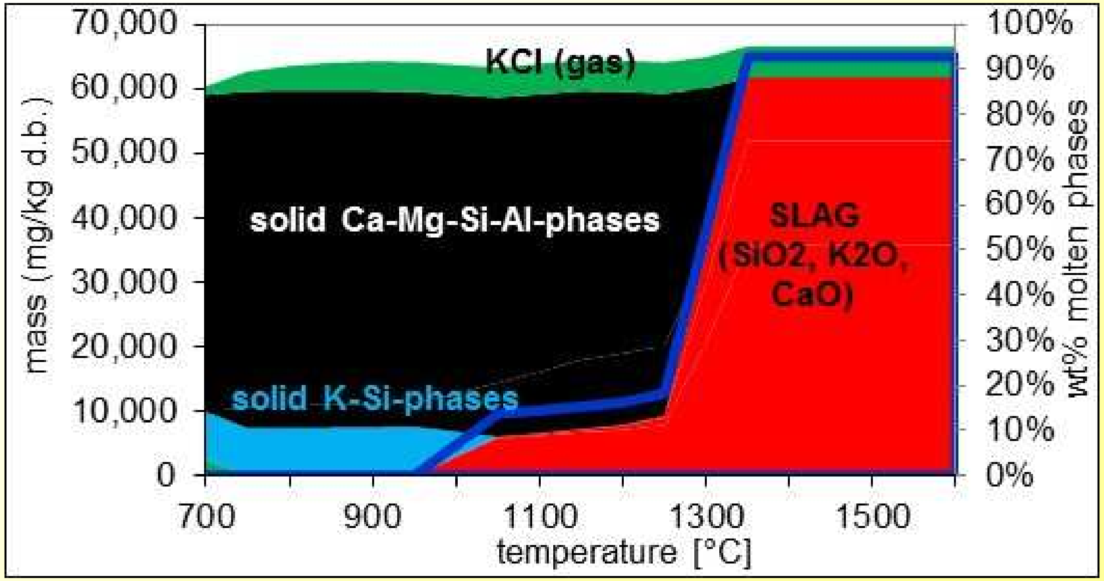


blue line: wt% of molten phases

mixture of 96 wt% wheat straw and 4 wt% kaolin



mixture of 96 wt% wheat straw and 4 wt% dolomite



Step 2: thermodynamic high temperature equilibrium calculations (TEC) (III)

- **Wheat straw:**
  - K-silicate compounds are relevant for the low ash melting temperatures.
  - They are transformed into molten phases (slags) at temperatures above 750°C.
- **Wheat straw + dolomite:**
  - The formation of solid phases containing Ca, Si, Mg and Al is preferred compared to the K-silicate compounds.
  - Therefore, the formation of the molten K-Si-compounds at 750°C is hindered and T30 increases to above 1,200°C.
  - The formation of Ca-silicates instead of K-silicates leads to an increased K release.
- **Wheat straw + kaolin:**
  - Formation of K-Al-Si-phases which remain solid also above 750°C.
  - Molten phases start to form above 950°C (T30 above 1,000°C).
  - A stronger embedding of K in the K-Al-Si-phases prevails resulting in a significantly reduced K-release.

➔ **TEC as a suitable tool to understand chemical reactions / compound formation of relevance and to select suitable additives; trends have been proven by experiments**

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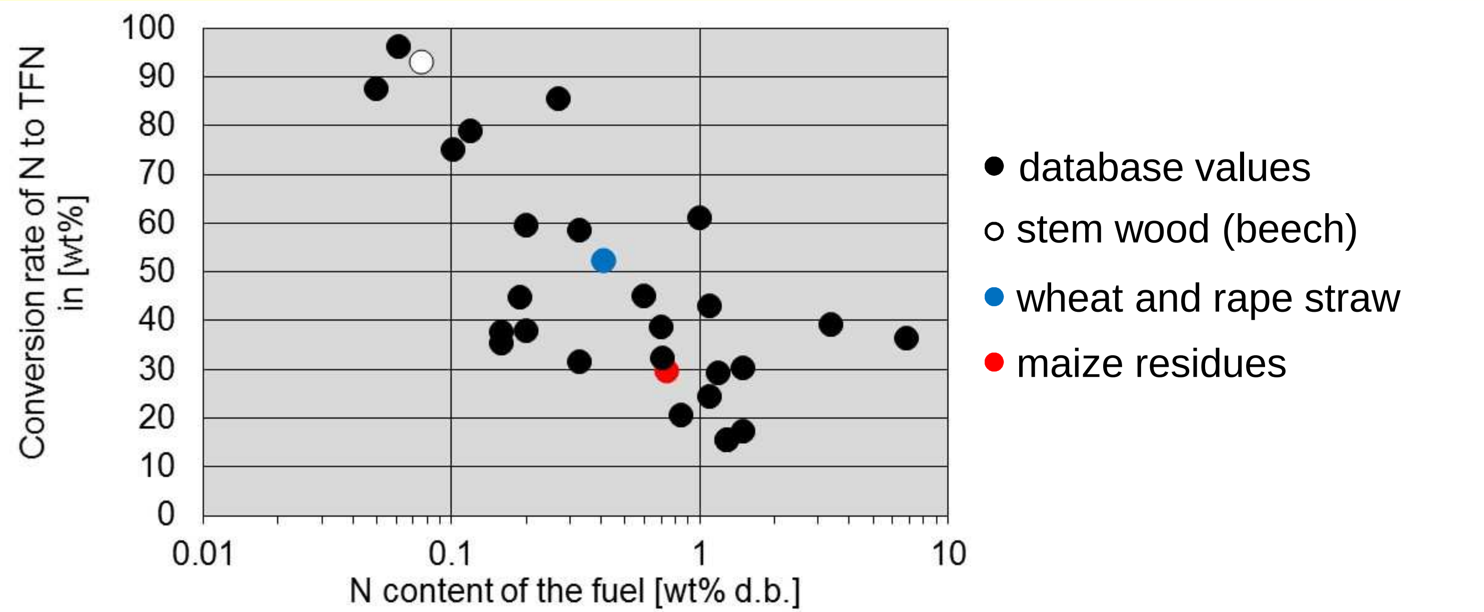
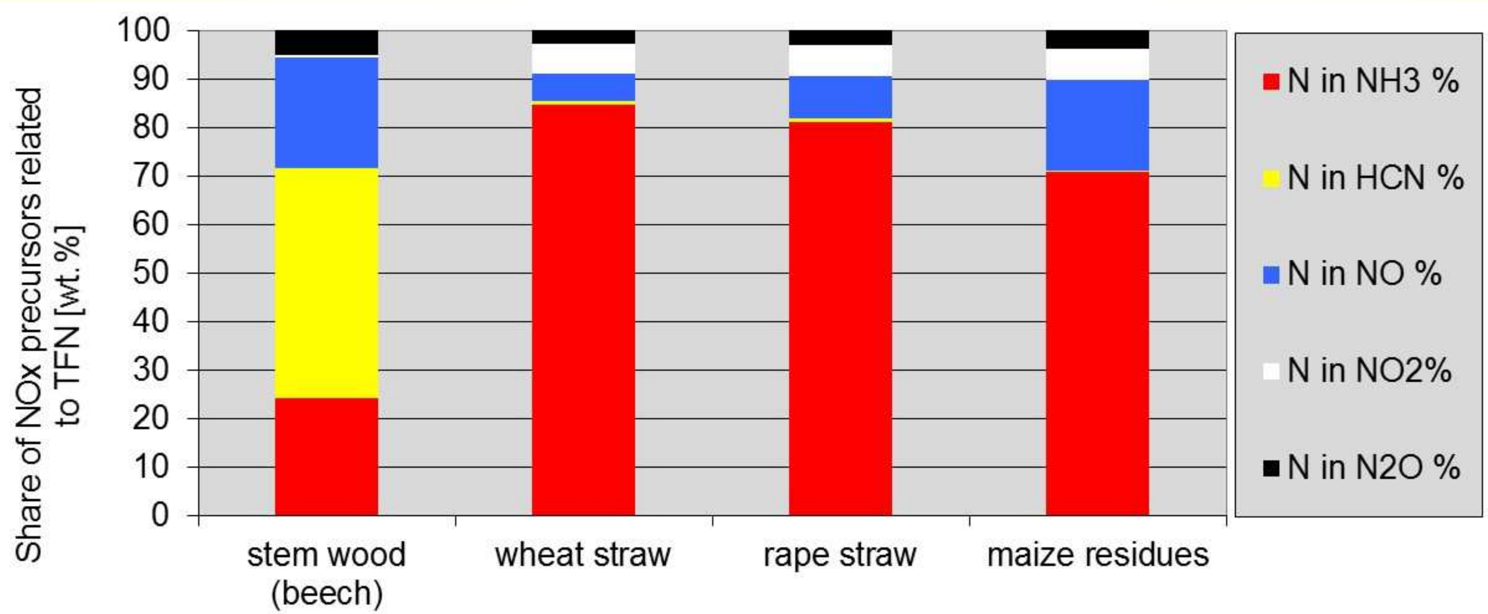
Step 3: results of lab-scale reactor tests – N-conversion



Explanations:

TFN = total fixed nitrogen (sum of N in NO, NH_3, HCN, NO_2 and N_2O)

Database values taken from the internal advanced fuel database of BIOS BIOENERGIESYSTEME GmbH, Graz (AT)



The release of NO_x pre-cursors can be determined

→ relevant for the prediction of NO_x formation

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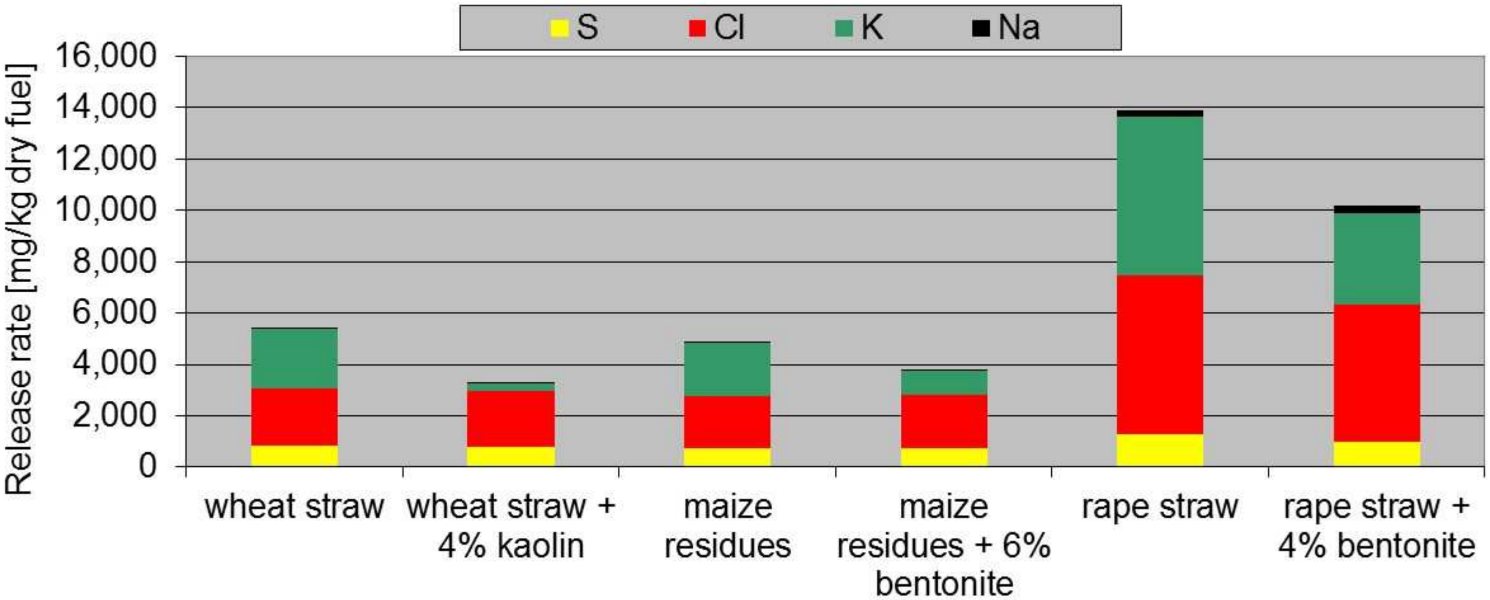
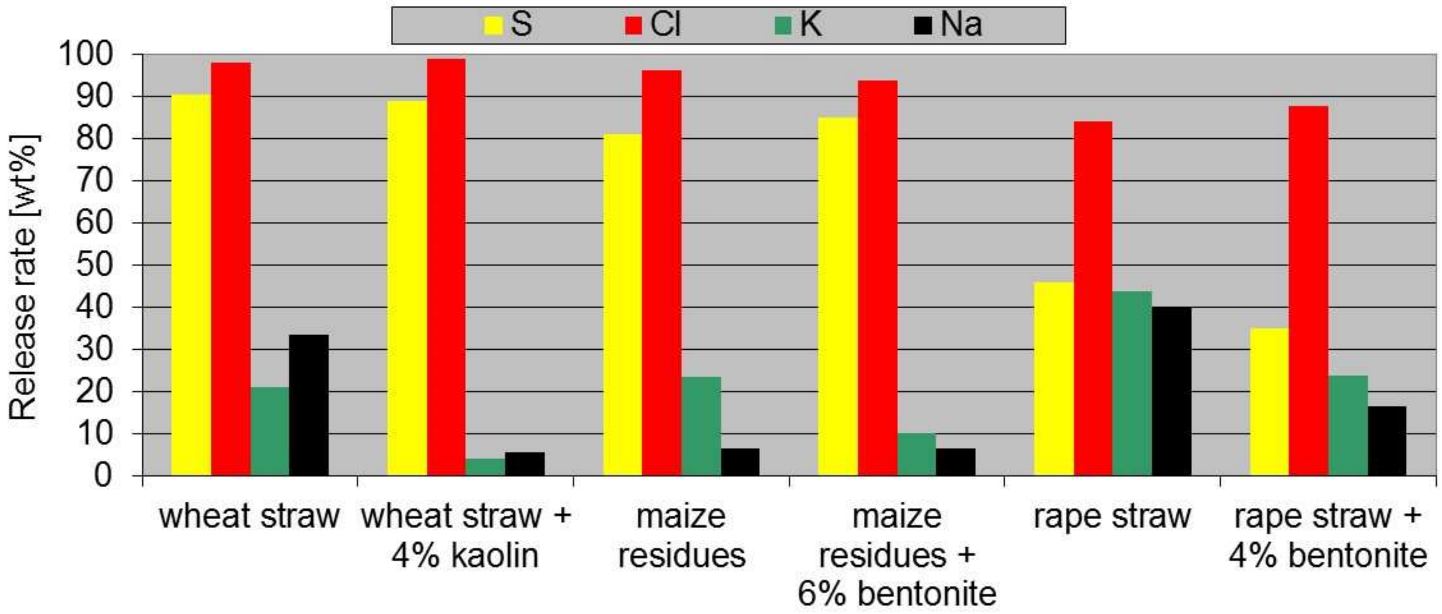
Step 3: results of lab-scale reactor tests – Release of S, Cl, K and Na





- **Quantitative information regarding inorganic element release can be gained**
- **The influence of fuel additive utilisation and fuel blending on inorganic element release can be studied**

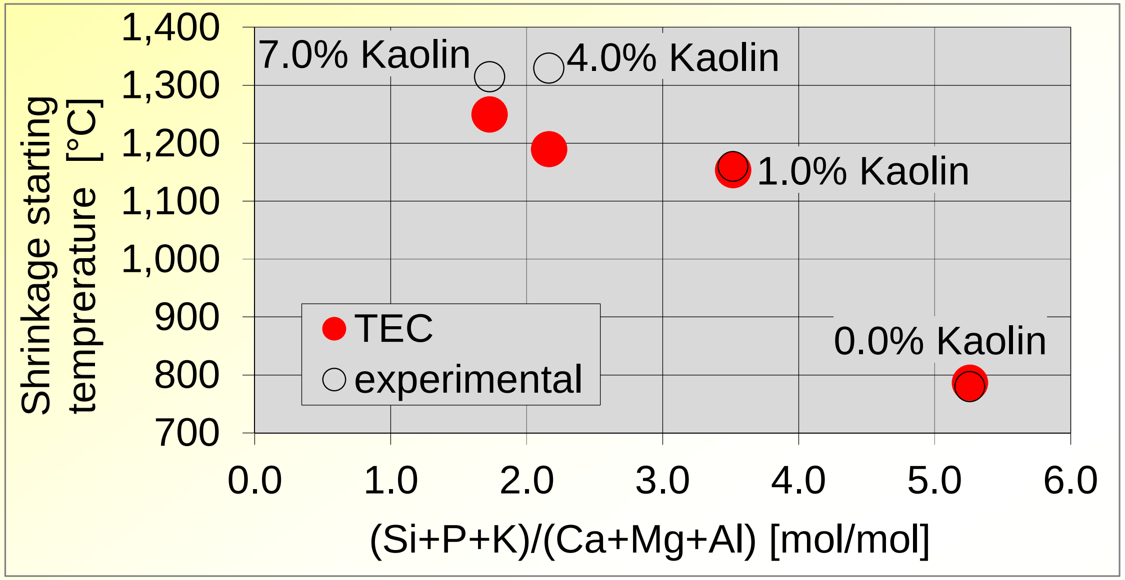
Explanations:

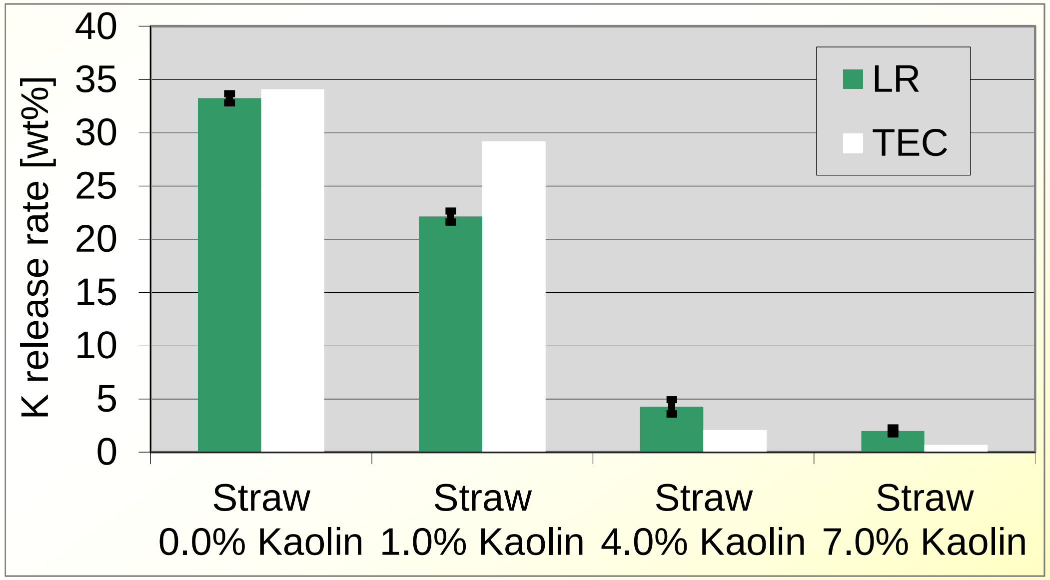
Release rate =

$$1 - \frac{element\ mass\ in\ the\ ash}{element\ mass\ in\ the\ fuel} * 100$$

Comparison with real-scale test run data (I)

Comparison of results from lab-scale reactor (LR) tests with results from TEC





- **Significant increase of the ash melting temperature with increasing kaolin addition**
- **K release decreases considerably with increasing kaolin addition**
- **Experimental results provide quantitative data and confirm the qualitative trends derived from TEC**
- **Suitability as well as meaningful amounts of additives can be evaluated**

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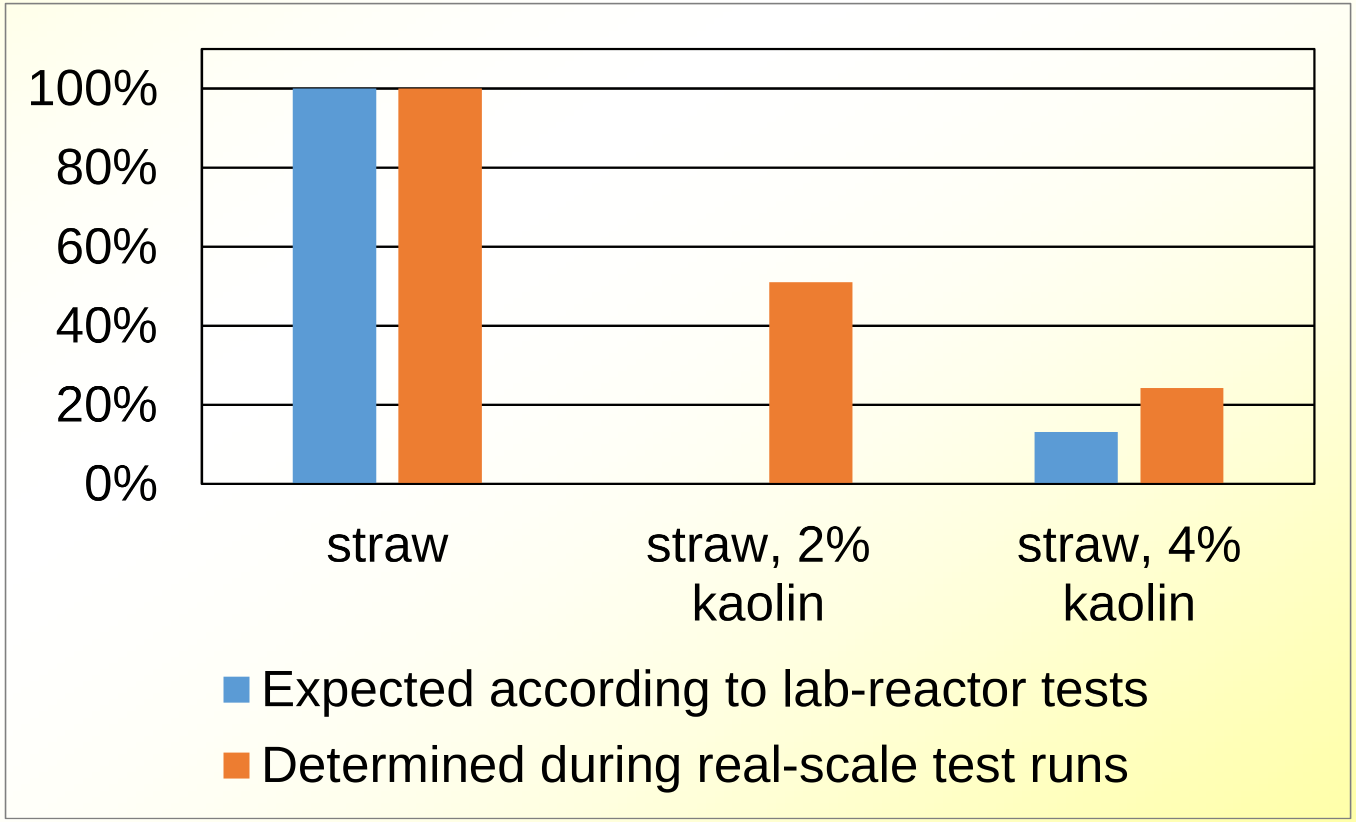
Comparison with real-scale test run data (II)

- **Results from test runs at a 180 kW$_{th}$ grate-fired combustion unit with**
  - **wheat straw pellets**
  - **wheat straw pellets containing 2 wt% and 4 wt% kaolin**

- **Aerosol emission reduction:**
  relative decrease of the aerosol emissions due to kaolin addition



Comparison with real-scale test run data (III)

Images of the grate ashes

wheat straw

wheat straw + 4 wt% kaolin

Summary and conclusions (I)

- A 3-step procedure for the application of advanced fuel characterisation tools for the combustion related assessment of biomass fuels, fuel blends and fuel/additive-mixtures has been developed.

- The procedure allows for a
  - quick and targeted assessment of combustion related fuel properties and
  - an assessment of influences of additives on these fuel properties

  at rather low efforts and risks compared to real-scale combustion tests.

- The procedure presented allows for a comprehensive fuel evaluation based on standard analyses as well as available software and equipment (reactors with functionalities comparable with the one presented exist).

- On demand it can also be supplemented by additional test methods to elucidate specific aspects (e.g.: SEM/EDX analyses, chemical fractionation tests, etc.)

Summary and conclusions (II)

- **Some relevant aspects have to be considered**
  - **The evaluation has to be done fuel specific**
    ➔ at least during the third step representative samples of the fuel of interest shall be utilised
  - **So-called problematic biomass fuels often show considerable variation ranges regarding their chemical composition**
    ➔ has to be considered when defining the additive ratio to be finally applied
- **Biomass fuel characterisation and evaluation according to the procedure presented can support**
  - **fuel selection for existing combustion plants**
  - **the design of new combustion plants**
  - **the development of strategies to improve the quality of a problematic biomass fuel by additive utilisation or fuel blending**

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