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Thermochemical modeling of the ash behavior of coals and biomasses/waste materials for co-utilization

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GTT Annuals Users Meeting 2018, Herzogenrath, Germany, 27-29 June 2018

OUTLINE

- Background
    - Substitute fuels
    - Ash properties
    - Ash related technical issues in power plants
- Materials and methods
    - Fuel samples
    - Thermochemical calculations
- Results and discussion
    - Mineral phases of pure fuels
    - Ash fusion behavior of fuel blends
    - Mineral phase behavior of fuel blends
- Summary and outlook

Substitute fuels

Wood and woody biomass
- wood
- sawdust
- etc.

Herbaceous and agricultural biomass
- grass and flowers
- straw
- stalks
- fibers
- shells and husks
- etc.

Aquatic biomass
- macroalgae
- microalgae
- uni-/multicellular species
- etc.

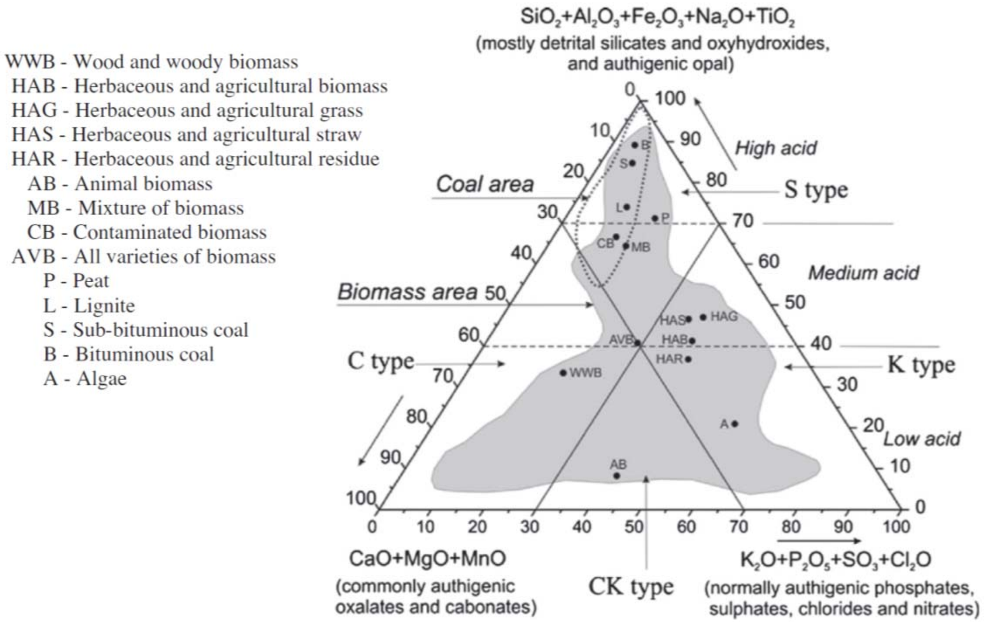
Animal and human biomass waste
- bone/meat meal
- manure
- etc.

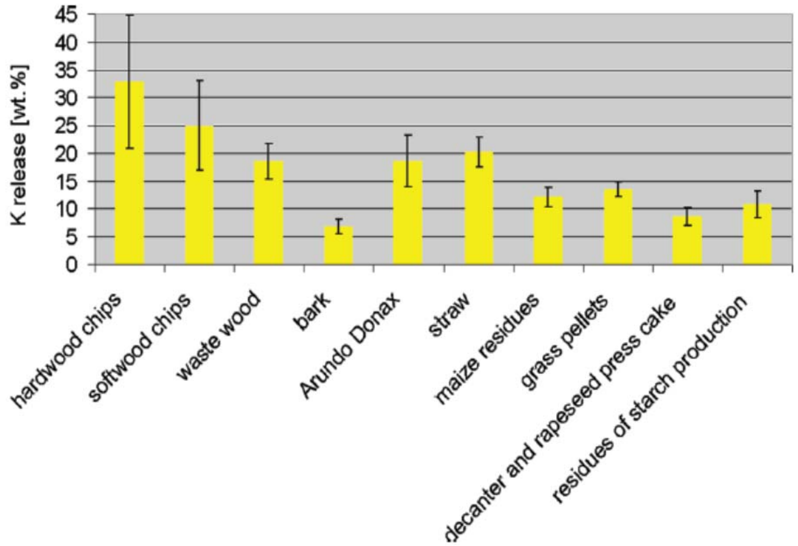
Contaminated biomass and industrial biomass wastes (semi-biomass)
- municipal solid waste
- refuse-derived fuels
- paper-pulp sludge
- railway sleepers
- etc.

Biomass mixtures
- blends of all mentioned biomass sources

S. V. Vassilev et al., Fuel, 94 (2012) 1-33.

Ash properties of the substitute fuels

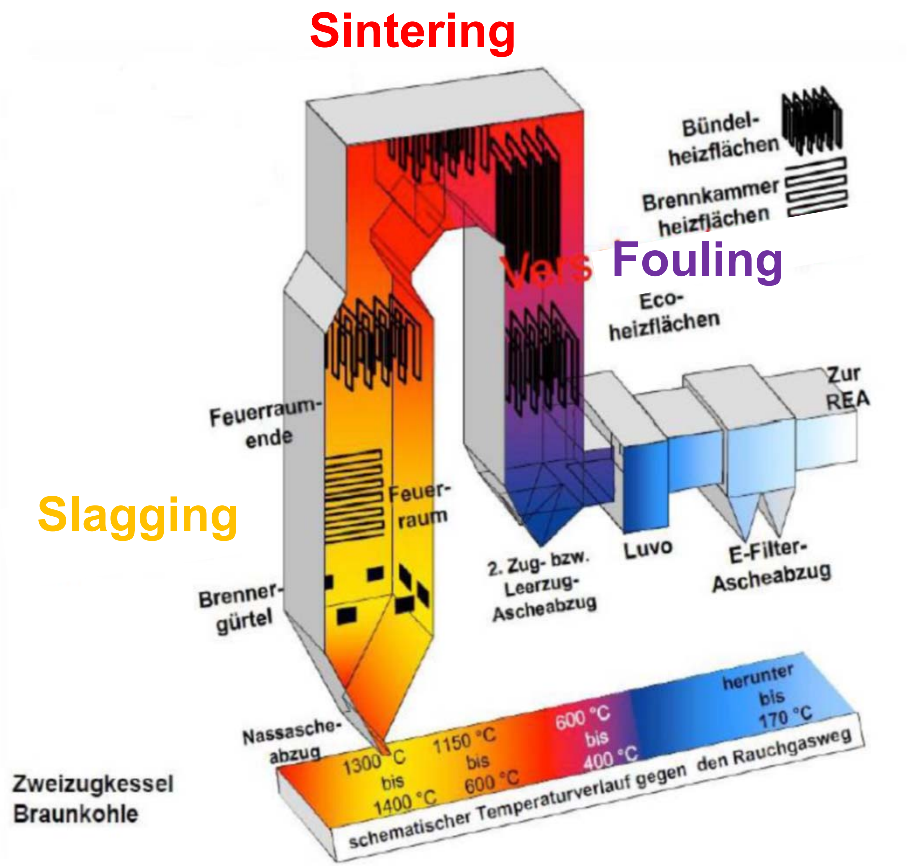


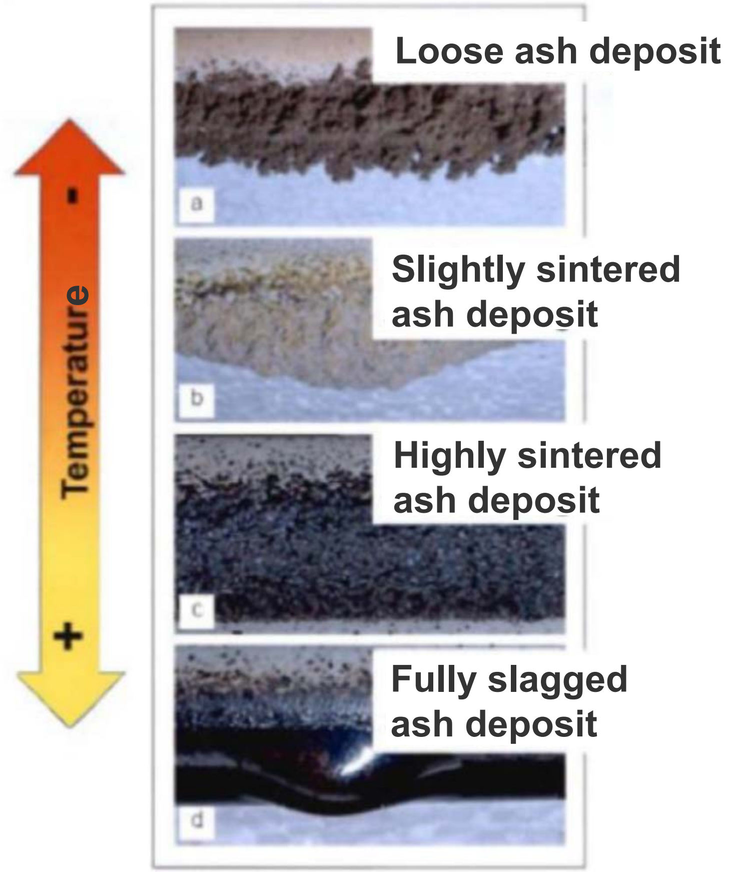


S. V. Vassilev et al., Fuel, 94 (2012) 1-33.

P. Sommersacher et al., Energy Fuels, 26 (2012) 380-390.

Ash related issues in power plants





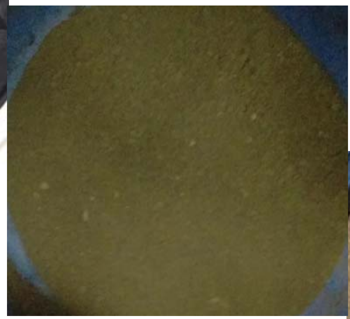
M. Muhammadie, PhD thesis, TU Bergakademie Freiberg, (2007).

M. Neuroth, RWE Power AG, personal communication.

Fuel samples

Substitute fuels

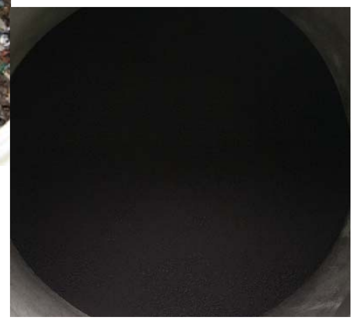
Columbian hard coal (CHC)



German brown coal mix (BCM)

Oat husks (OAT)

Refuse-derived fuel (RDF)



Sewage sludge (SWS)

Regular fuels

Thermochemical calculations

- FactSage™ version 7.0
- Equilib module

C. W. Bale et al., Calphad, 54 (2016) 35-53.

- Data bases (in the order specified): FToxid, FTmisc, FTsalt, and FactPS
- Solution species: SlagA, AMonoxide, M2O3(Corundum), AMullite, ASpinel, AWollastonite, AMelilite, AOlivine, ACordierite, AOrthopyroxene, Ca(Al,Fe)2O4, Ca2(Al,Fe)2O5, Ca3(Al,Fe)2O6, Ca(Al,Fe)6O10, Ca(Al,Fe)12O19, NaAlO2-HT, (Ca,Na2)Ca8Al6O18, Ca2(Al,Fe)8SiO16, Na,K,[Rb,Cs]//NO3(ss), FeS-liq, AMatte, Ca3Ti2O7-Ca3Ti2O6, and AlkCl-ss_rocksalt
- Input data: stoichiometric ash composition from XRF (except of CO_2 and trace elements)

  atmosphere: artificial air using 20-fold mass of ash

  composition of artificial air: N_2, O_2, and Ar
- Pressure: 1 atm
- Analysis: 1) mineral phases at 815 °C

  2) liquidus temperature (T_{liq}) defined by the temperature with 1 wt.% of remaining solid fraction

Ash composition (ashing at 815 °C)

Oxides	CHC	BCM	OAT	RDF	SWS
Normalized mass fraction (XRF) / wt.%					
CO_2	0.21	0.41	0.49	0.72	0.26
Na_2O	0.74	0.04	0.61	1.74	0.54
MgO	1.41	2.32	2.72	1.73	3.88
Al_2O_3	22.58	0.42	0.32	12.04	9.25
SiO_2	59.67	57.73	65.38	53.11	41.48
P_2O_5	0.09	0.01	7.03	0.62	16.99
SO_3	0.85	15.36	2.54	3.75	1.09
K_2O	2.04	0.08	16.93	0.90	1.63
CaO	2.00	15.36	3.28	18.90	9.65
TiO_2	0.96	2.13	0.02	1.65	1.28
Fe_2O_3	9.03	5.90	0.39	3.87	13.42
Traces	0.42	0.24	0.29	0.97	0.52
Base-to-acid ratio (oxidizing) / -					
B/A (mass)	0.18	0.39	0.33	0.40	0.42

$$\frac{B}{A} = \frac{CaO + MgO + Na_2O + K_2O + Fe_2O_3}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5}$$

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Mineral phases of Columbian hard coal (ashed at 815 °C)

Mineral phase	Stoichiometry	HTA	FactSage™ (HTA)
Amorphous	–	55	0
Mineral phases (normalized)/wt%			
Sulfates			
Gypsum	$CaSO_4{\cdot}2H_2O$	–	–
Anhydrite	$CaSO_4$	4	4
Simple oxides			
Corundum	Al_2O_3	–	–
Quartz	SiO_2	48	27
Maghemite	$\gamma{-}Fe_2O_3$	1	9
Hematite	Fe_2O_3	10	
Silicates			
Kaolinite	$Al_2Si_2O_5(OH)_4$	–	–
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	31	–
Mullite	Al_4SiO_8/Al_2SiO_5	5	21
Albite	$NaAlSi_3O_8$	2	10
Sanidine	$KAlSi_3O_8$	–	12
Cordierite	$Al_3Mg_2Si_5O_{18}$	–	13

M. Reinmöller et al., Fuel, 202 (2017) 641-649.

Mineral phases of RDF (ashed at 815 °C)

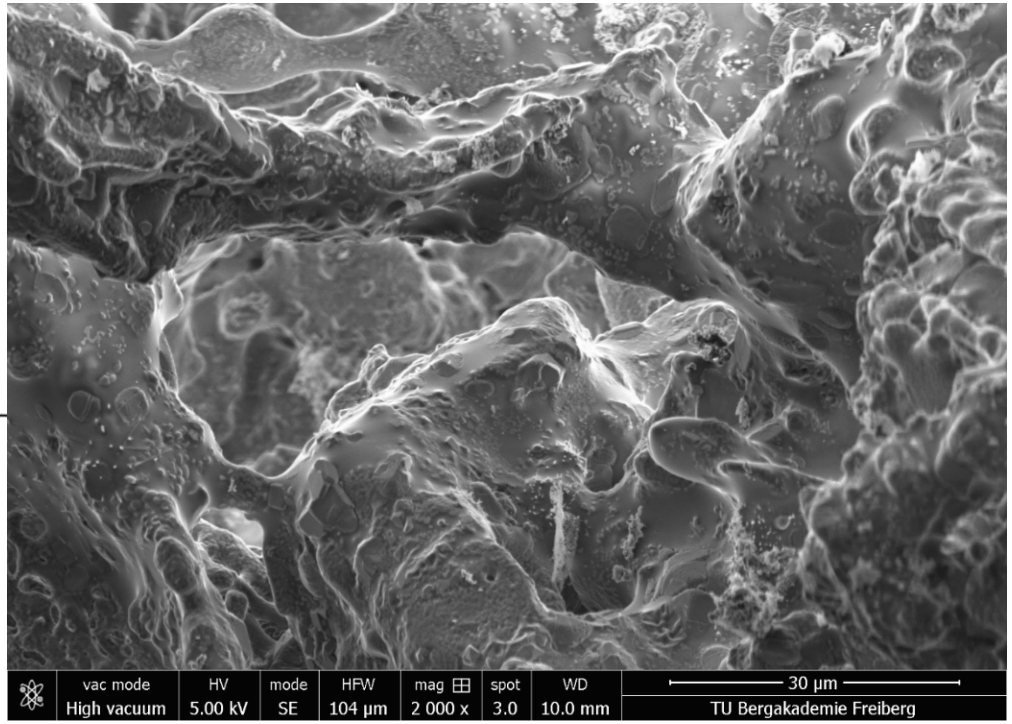
Mineral phase	Stoichiometry	HTA	FactSage™ (HTA)
Amorphous	–	15	0
Mineral phases (normalized)/wt%			
Sulfates			
Gypsum	$CaSO_4 \cdot 2H_2O$	–	–
Anhydrite	$CaSO_4$	2	8
Carbonates			
Calcite	$CaCO_3$	1	–
Dolomite	$CaMg(CO_3)_2$	–	–
Simple oxides			
Corundum	Al_2O_3	4	–
Quartz	SiO_2	33	–
Cristobalite	SiO_2	1	–
Maghemite	Fe_2O_3	–	–
Hematite	Fe_2O_3	–	–
Magnetite	Fe_3O_4	–	–
Rutile	TiO_2	–	–
Silicates			
Kaolinite	$Al_2Si_2O_5(OH)_4$	–	–
Wollastonite	$CaSiO_3$	18	12
Diopside	$CaMgSi_2O_6$	8	12
Andradite	$Ca_3Fe_2Si_3O_{12}$	18	12
Anorthite	$CaAl_2Si_2O_8$	7	16
Jasmundite	$Ca_{11}Si_4O_{18}S$	–	–
Hauyne	$Na_3CaAl_3Si_3O_{12}(SO_4)$	8	–
Albite	$KAlSi_3O_8$	–	26
Sanidine	$NaAlSi_3O_8$	–	7
Titanite	$CaTiSiO_5$	–	5
Other mineral phases			
Aluminum	Al	–	–
Copper	Cu	–	–
Graphite	C	–	–
Halite	NaCl	–	–
Whitlockite	$Ca_3P_2O_8$	–	2

M. Reinmöller et al., Fuel, 202 (2017) 641-649.

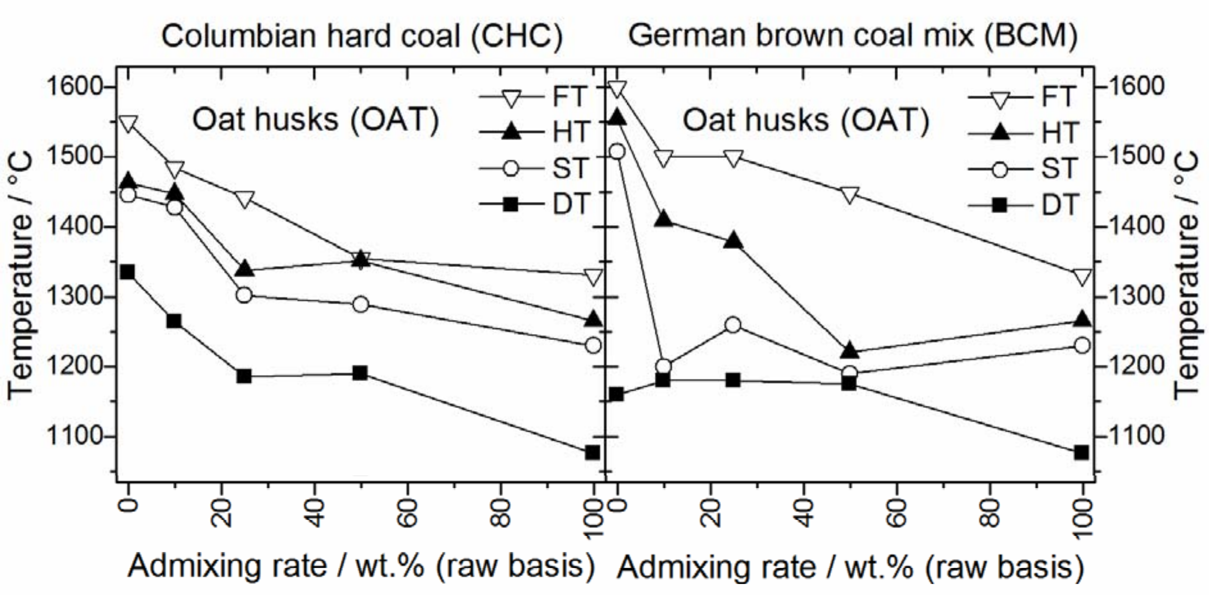
Mineral phases of oat husks (ashed at 815 °C)

Mineral phase	Stoichiometry	HTA	FactSage™ (HTA)
Amorphous	–	50	60
Mineral phases (normalized)/wt%			
Sulfates			
Arcanite	K_2SO_4	12	17
Carbonates			
Calcite	$CaCO_3$	–	–
Magnesite	$MgCO_3$	1	–
Huntite	$CaMg_3(CO_3)_4$	1	
Simple oxides			
Corundum	Al_2O_3	–	
Quartz	SiO_2	10	
Cristobalite	SiO_2	48	
Iron oxide	Fe_2O_3	–	
Silicates			
Enstatite	$Mg_2Si_2O_6$	–	
Microcline	$KAlSi_3O_8$	16	
Phosphates			
Struvite	$KMgPO_4{\cdot}6H_2O$	–	
Berlinite	$AlPO_4$	5	
Ca-Mg-phosphate	$Ca_3Mg_3(PO_4)_4$	–	
Magnesium phosphate	$Mg_3P_2O_8$	–	

M. Reinmöller et al., Fuel, 202 (2017) 641-649.

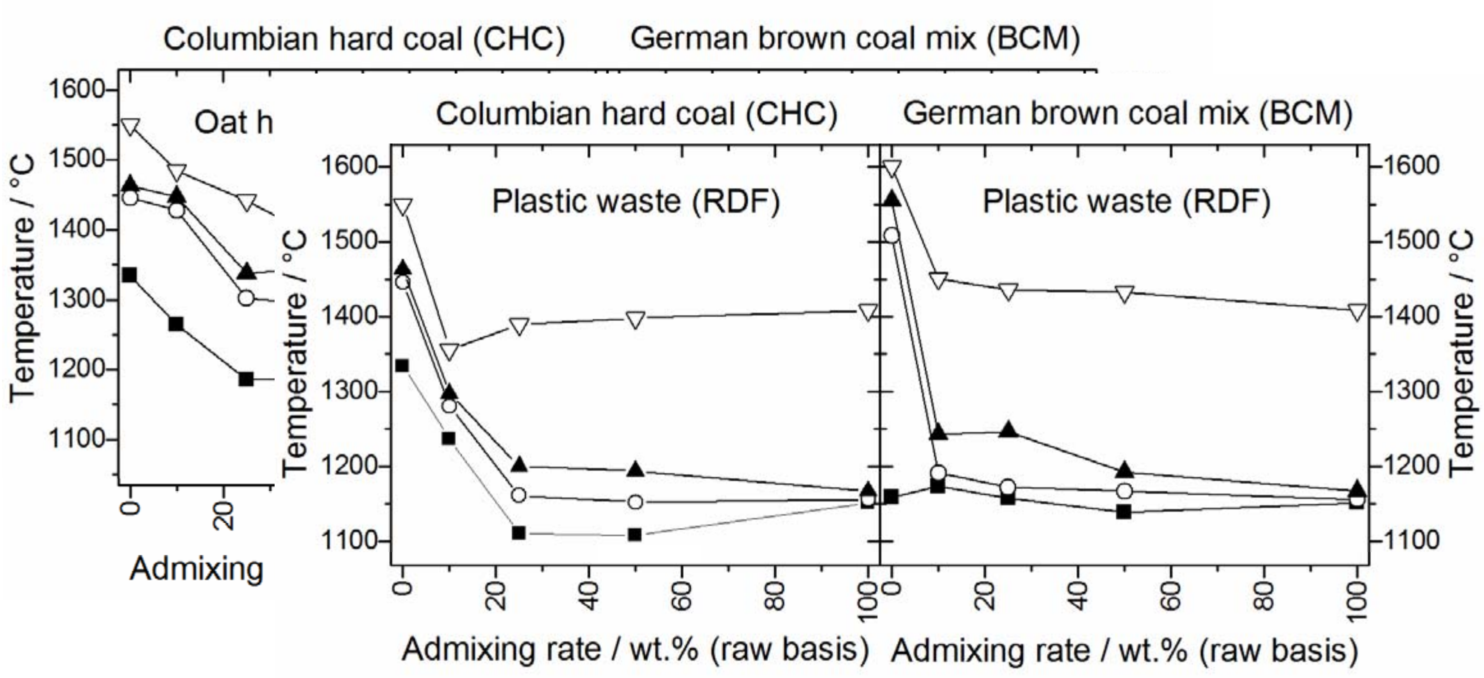


Experimental ash fusion (OAT addition, ashed at 815 °C)



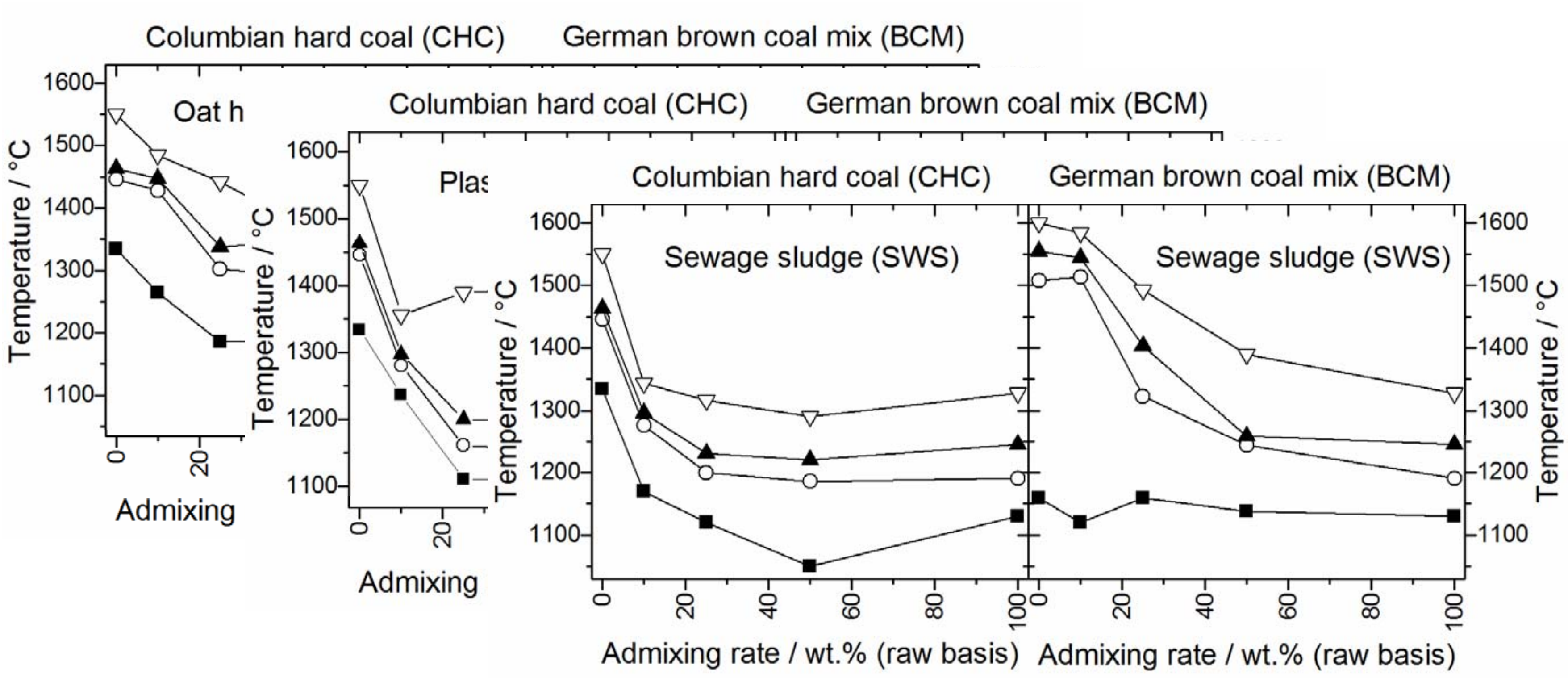
- Continous change of ash fusion temperatures with admixture rate of oat husks

Experimental ash fusion (RDF addition, ashed at 815 °C)



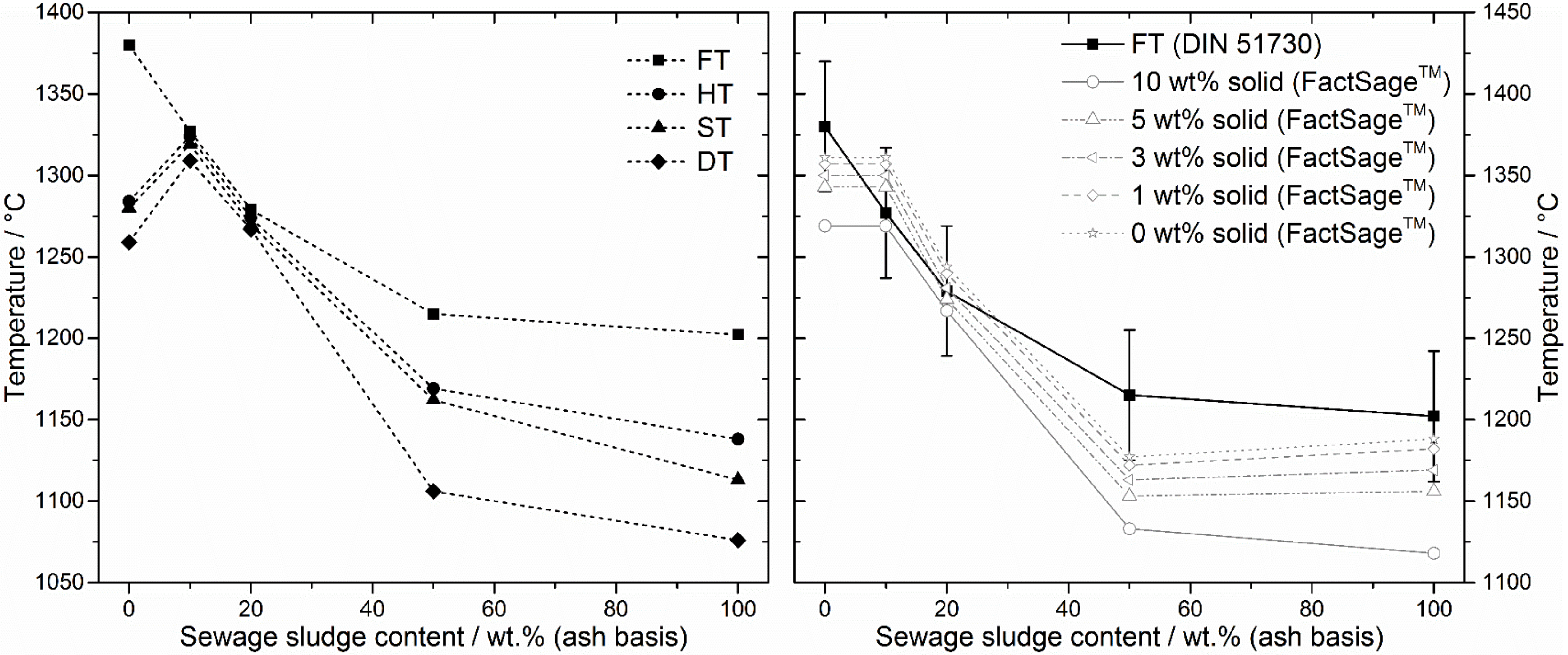
- Strong change of ash fusion temperatures at low admixture rates of RDF
- At 10 wt.% (BCM:RDF) and 25 wt.% (CHC:RDF) the ash fusion temperature already reached the values close to pure RDF

Experimental ash fusion (SWS addition, ashed at 815 °C)



- Strong decrease of the ash fusion temperatures to values of sewage sludge (CHC:SWS)
- Continous change with increasing admixture rates (BCM:SWS)

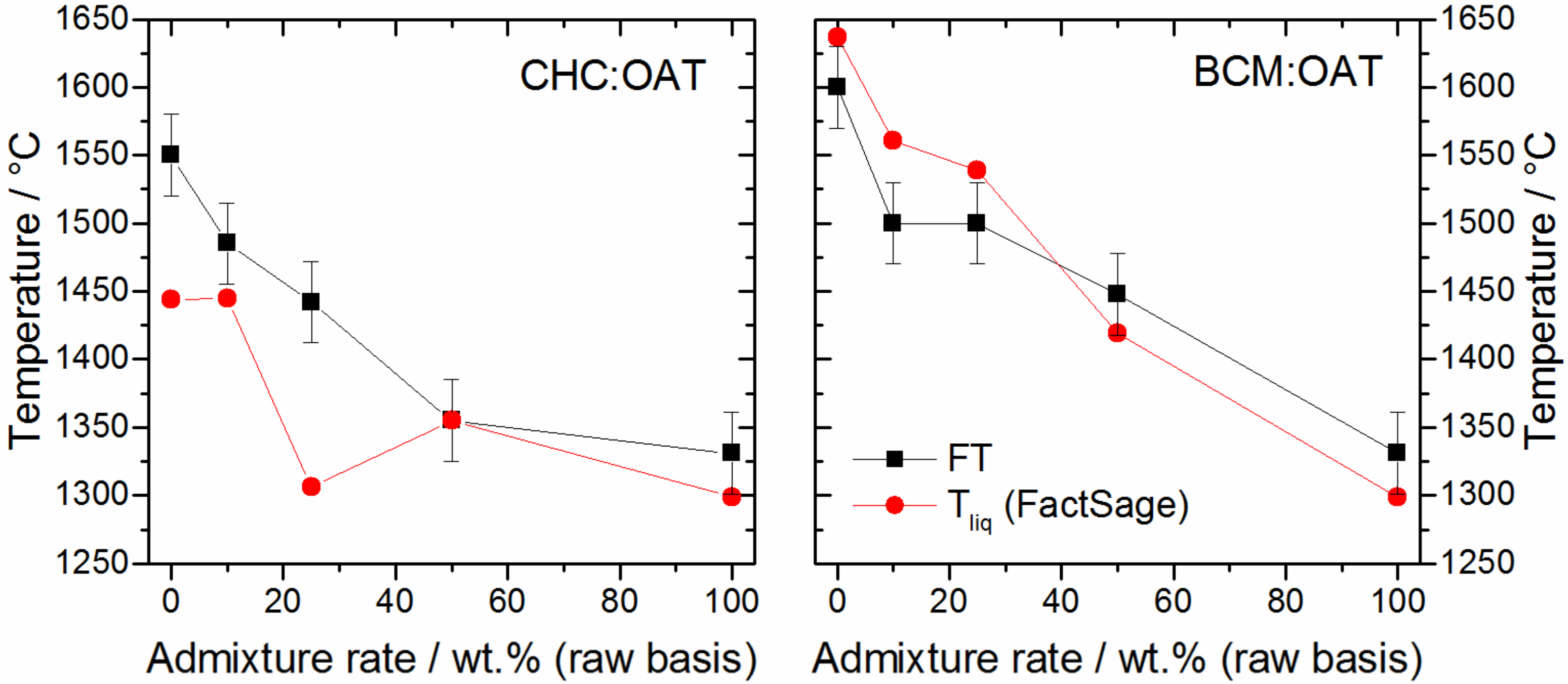
Calculation approach for the flow temperature



D. Schwitalla et al., Fuel Processing Technology, 175 (2018) 1-9.

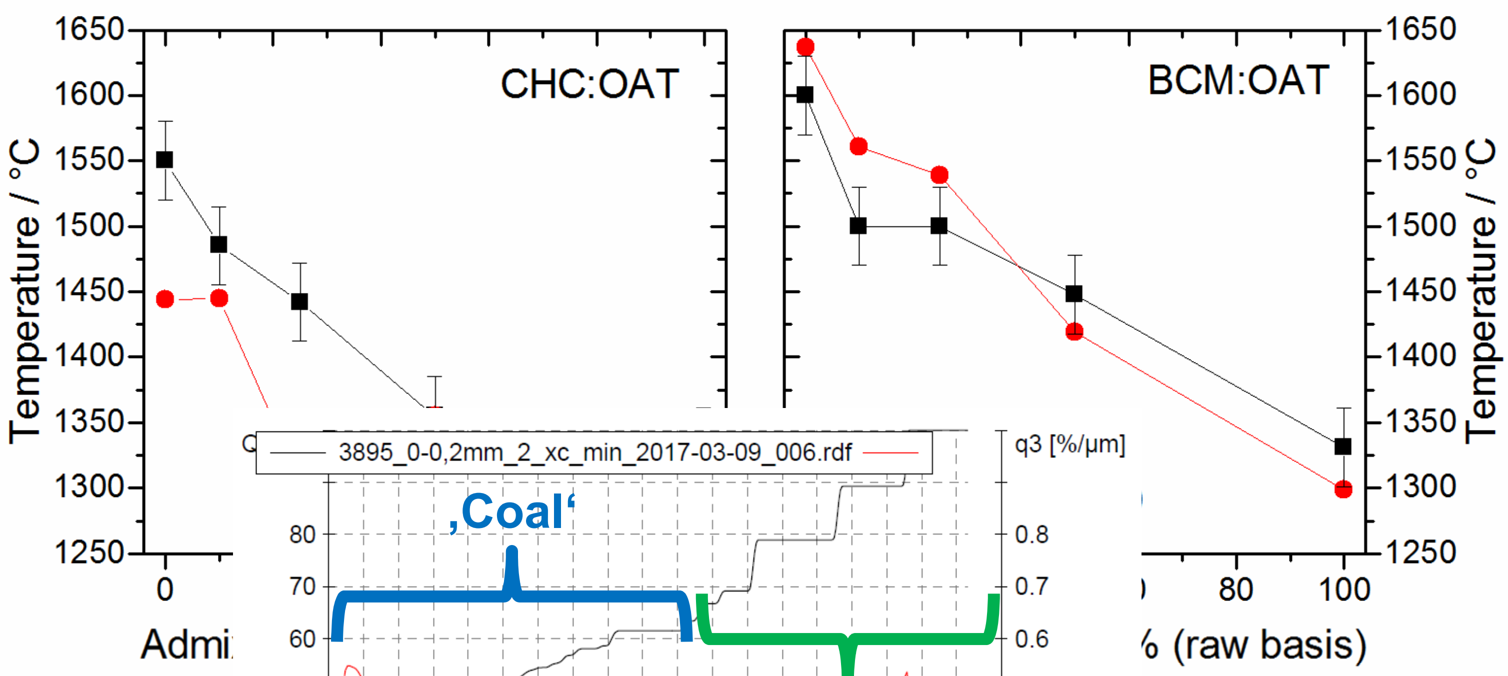
- FactSage™ is able to reproduce the flow temperature very well from the amout of residual solid ash
- Best agreement is achieved for a residual mass of 1 wt.% solid fraction

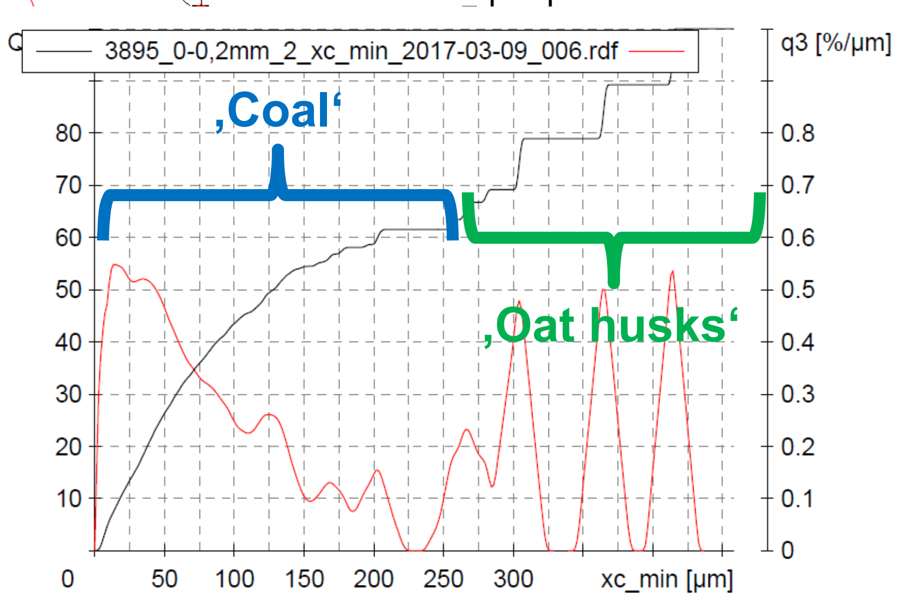
FactSage™ calculations (OAT addition, ashed at 815 °C)



- Trends of the flow temperatures are reproduced by FactSage™
- But strong fluctuations for CHC:OAT (cf. mineral phase composition)

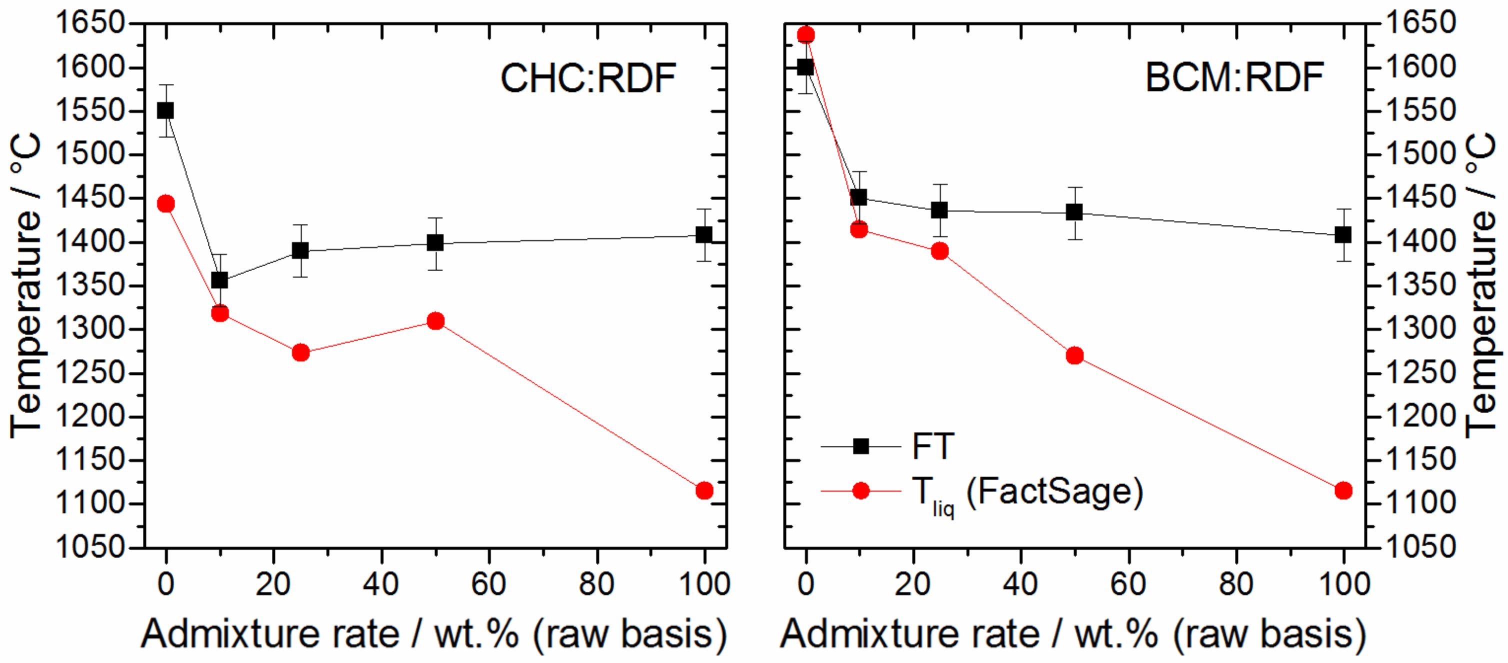
FactSage™ calculations (OAT addition, ashed at 815 °C)





- Trends (
- But stro ition)

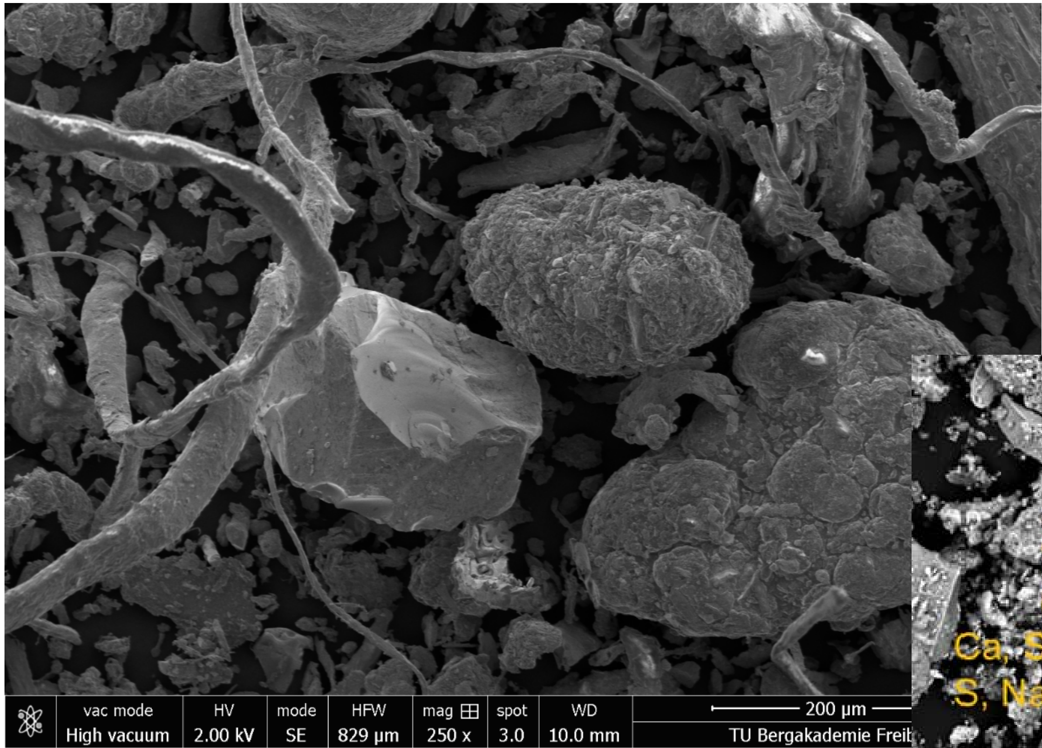
FactSage™ calculations (RDF addition, ashed at 815 °C)

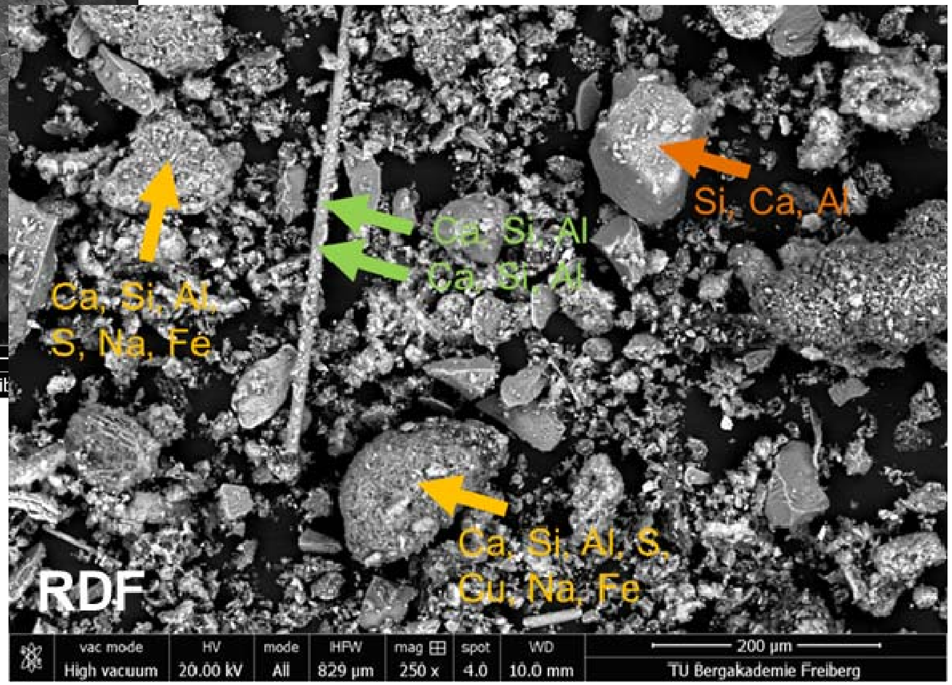


M. Reinmöller et al., in preparation

- Agreement at least for low additions of RDF
- FactSage™ fails for higher admixture rates

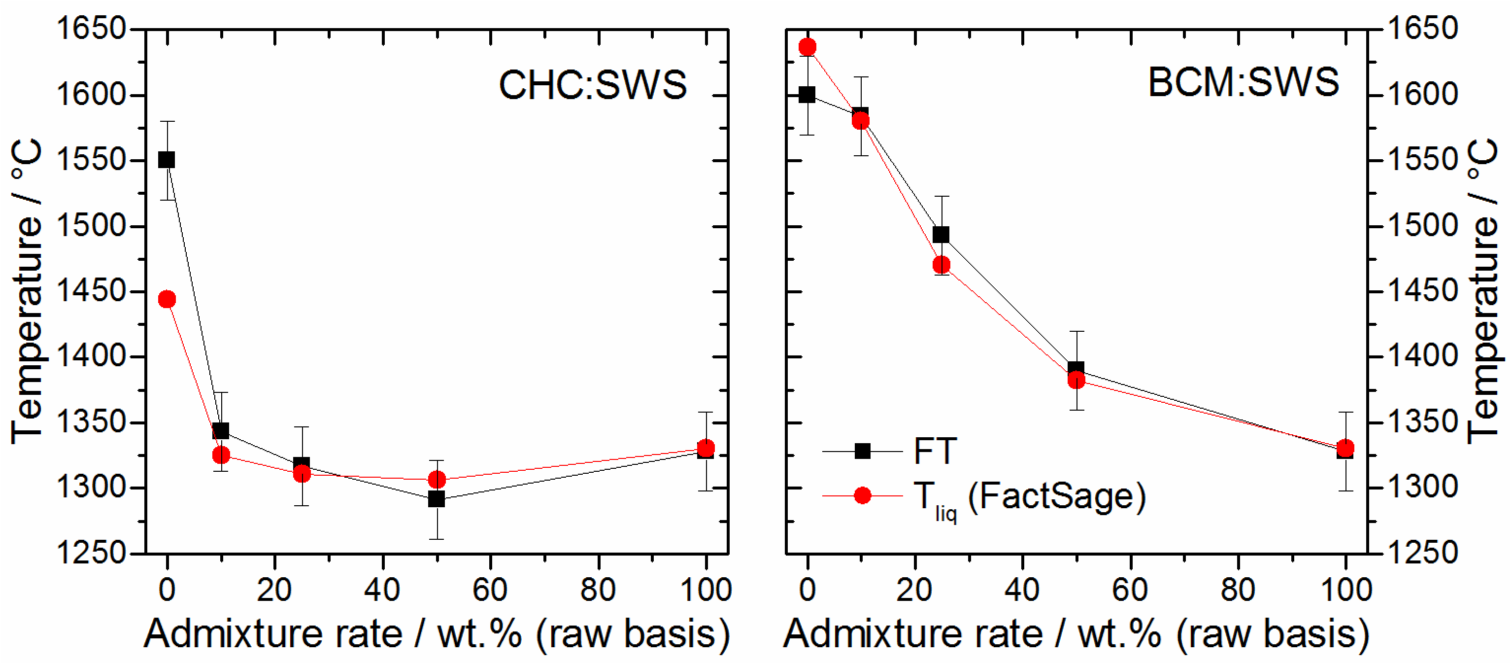
FactSage™ calculations (RDF addition, ashed at 815 °C)





M. Reinmöller et al., submitted

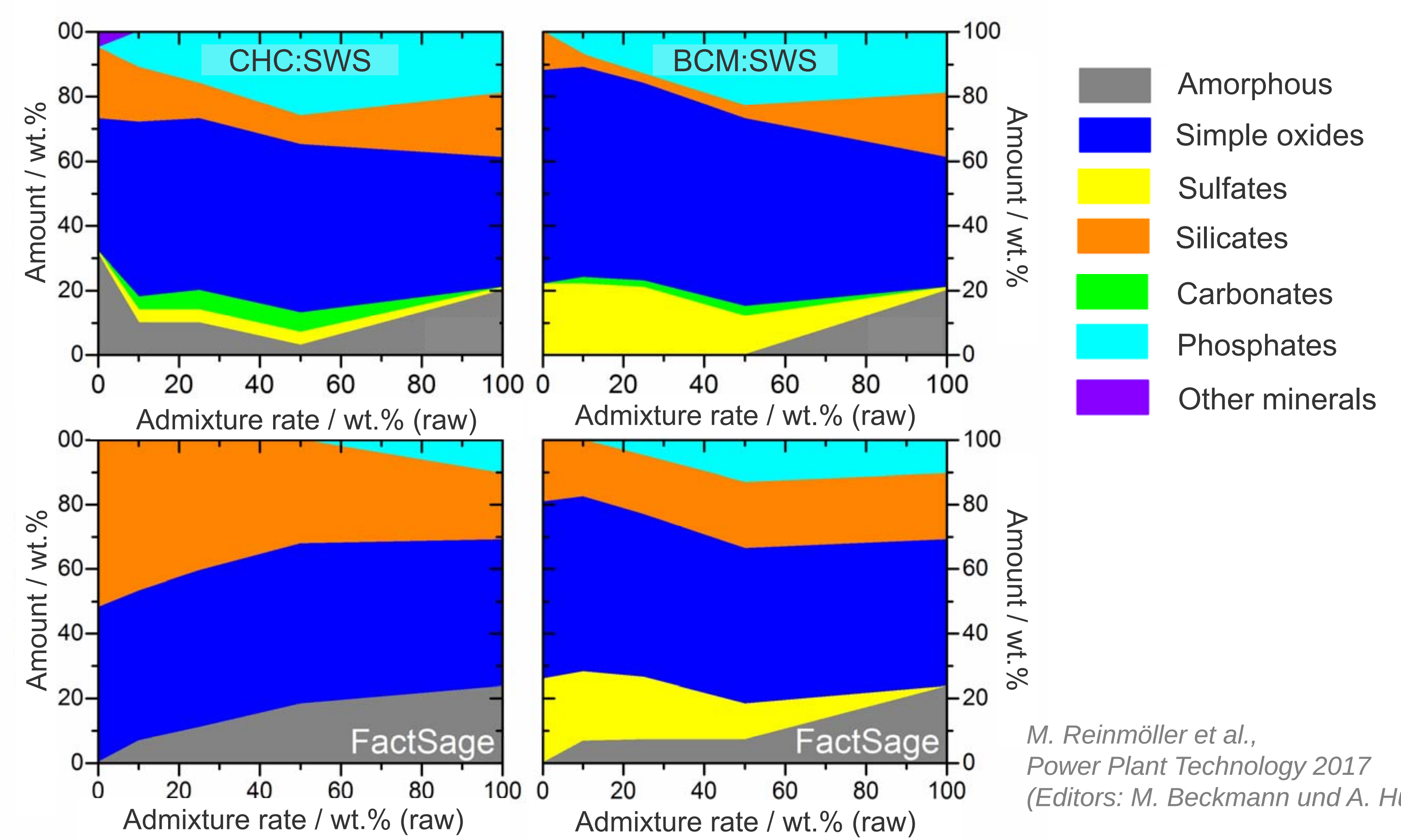
FactSage™ calculations (SWS addition, ashed at 815 °C)



- FactSage™ fits the experimental values well

M. Reinmöller et al., Kraftwerkstechnik 2017 (Hrsg.: M. Beckmann und A. Hurtado).

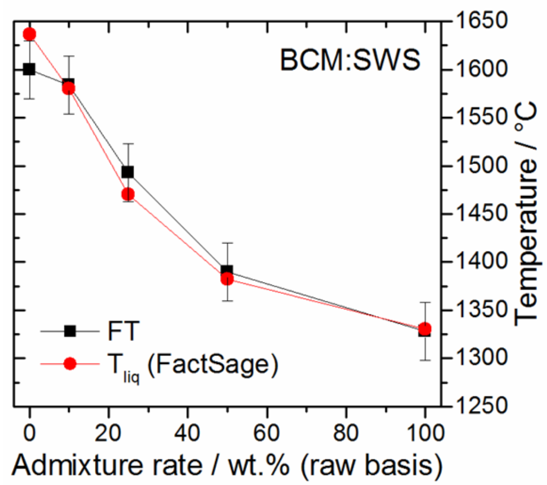
FactSage™ calculations (SWS addition, ashed at 815 °C)



M. Reinmöller et al.,
Power Plant Technology 2017
(Editors: M. Beckmann und A. Hurtado).

Summary

- FactSage™ calculations are suitable for prediction of:
  - Mineral phase compositions of single fuels from XRF results
  - Ash fusion behavior of fuel blends
  - Mineral phase composition of fuel blends
- FactSage™ calculations resulted in good agreement for homogeneous ash samples



- Calculations can fail due to limitations, e.g. heterogeneity, spatial distribution and limited transport

Outlook

- Modeling of the release of ash species causing fouling (e.g. K_2O)
- Utilization of the GTOX data base for FactSage™ calculations

ACKNOWLEDGEMENT

The support of these studies by
RWE Power AG is gratefully acknowledged.

Thank you very much for your kind attention!