Thermochemical equilibrium modeling of ash transformation during the thermal conversion of different biomass types with a focus on the speciation of P and K

ARASID

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- Practical Setup
 - Reactor system, mass balance, fuel parameters
- Databases
 - GTOX, SGPS, FactPS, FToxid, FTsalt
- Input Parameters
 - Fuel composition, temperature, gas conditions
- Data Extraction & Evaluation
 - Phase distribution, melt formation, precipitation, gas release



Reactor System

- Macro-TGA
- Continuous gas inlet (7 L/min)
- Temperature: 600 950°C
- Residence time: 10 240 min
- Quenching zone
- Sample size: 700 mg



Fuel Parameters



- Bark & poplar: Ca, K, P
- Wheat straw: Si, K, Ca
- Grass: K, Si, Ca
- Wheat grain: P, K, Mg
- Twigs: Si, Ca, K
- Ash content: 2.2 8.5 wt.% df

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Fuel Parameters



- Sewage sludge: Si, P, Fe, Ca, Al
- Sunflower husks: K, Ca, Mg, (S)
- Wheat straw: Si, K, Ca
- Ash content: 3 33 wt.% df
- Mixtures based on P/K-ratio



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Research Goals - Motivation

- Research motivation
- Closing the anthropogenic P-cycle
- Make use of potential K-rich residue wastes
- Research gaps
- Phosphate alteration Ca-P \rightarrow K-(Ca)-P
- Influence of the process parameters

- Thermochemical calculations:
- Phases in condensed ash phases $f(T, x_i)$
- Melt formation $f(T, x_i)$
- Precipitated phases from molten ash
- Release rates (K, Na, Cl, S, P)
- Practical equilibrium state



Databases & Input Parameters

• Databases

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- FactPS/oxide/salt (carbonate melt structures, for cation-rich fuels)
- SGPS (compatibility with GTOX in complex systems)
- GTOX (complexity of the phosphate-compounds enhanced)
- Super-stoichiometric gas input without set activities
- Linear ash element manipulation (α)
- Temperature 600–1200°C
- Simulation of λ -value for gas conditions



Condensed Phases $-f(T, x_i, p_i)$

- Cation-dominated fuels
 - Usage of salt melt database required
 - Carbonate structures & melt
 - Gasification mostly affects volatilization

- Anion-dominated fuels
 - Complex compound & SS-system
 - Oxide melt triggered by Si/P-availability
 - Gasification may influence oxidation state



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Initial Melt Formation $-f(x_i, p_i)$

• Low IMT for pure SS

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- Caused by excess $P \rightarrow$ Fe-phosphates
- Gasification: $Fe^{3+} \rightarrow Fe^{2+}$

- Diverging trends WS-SH mix
 - Driven by K-silicate melt formation
- Little impact of gasification



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Melt Development – f(T)



- SS:
 - Low IMT, but flat gradient
- WSS:
 - rapid complete melting in pure WS
 - T-shift & gradient flattening in mixtures

• SSH

• Significant volatilization of K in pure SH

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• T-shift mostly due to Si-availability



Phosphorus Speciation – $f(x_i, p_i)$



- Phosphates grouped by literature
 - Based on potential plant availability
- K-phosphates highly favored
 - Strong stability hierarchy indicated
- (Ca, Mg)-phosphates most T-stable
 - Other phosphates more melt-affine



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Melt Precipiation $- f(x_i, p_i)$

- Equilibrium cooling
- Melt provides benefits
 - K-enriched at lower T
 - K-phosphates preferred over K-silicates
- SS-rich ashes (80 wt.%) suitable
 - 50% melt suffices for K-phosphates





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Condusio

- Database & element selection is the most crucial step
- Thermodynamics favor our goal of P-alteration
- Melting behavior changes dependent on mixture
 - WS-mix: Increased melting-T (inhibited K-silicate formation)
 - SH-mix: Decreased melting-T (enhanced P-Si-melt formation)
- High affinity of P and K towards the melt (amorphous)
- Guideline for experimental design and interpretation



Unsolved Issues

- Hydroxy-apatite as stoichiometric compound
- Complexity of the whitlockite system
- Cation/Anion-ratio requires database adaption
- Systems with gas flow & volatile compounds (S)
- Hierarchy in the formation of stoichiometric compounds
- Viscosity parameters for (Si/P/Fe)-rich slags

→ Uniform Methodology



Thank you for your attention

Handan

Any questions to be answered?

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