Thermodynamic modeling of biomass combustion and ash chemistry applications

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EU-27, gross inland energy consumption
Primary raw materials

Source: European Commission’s Market Observatory data for 2008
Biofuels – Waste derived fuels – “Opportunity fuels”

- Woodchips
- Saw dust
- Bark
- Forest residues
- Annual crops
- Prunings
- Shells, husks & hulls
- Olive stones
- Biorefinery residues
- Pulp & paper process by-products
- Refuse derived fuels (RDF)
- Waste sludges
- Recovered waste wood
- Meat and bone meal
- Chicken litter
Ash Forming Matter in Biomass Combustion – Research Topics

- Characterization of AFM
- Release of AFM in furnace
- Fly Ash Formation
- Bed/Grate Reactions
- Fouling
- Superheater Corrosion
- Understanding Fuel Mixtures
Fouling and corrosion due to unsuitable fuel mix
Thermodynamic modeling & Ash chemistry

- Ash deposition
- Bed agglomeration
- Furnace slagging
- Superheater corrosion
- Trace element emissions
- Black liquor combustion
Example
Black liquor recovery boiler
Kraft Pulping Process

Wood → Lignin → Fibre

White Liquor (NaOH + Na₂S) + Fibre → Black Liquor

155°C 900 kPa
A 1000 t/d Kraft Pulp Mill produces 1500 t/d BL d.s.

8000 ~ 10,000 t/d weak black liquor
**As-Fired Black Liquor Composition (750 liquor samples; All Wood Species)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Typical</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content, %</td>
<td>72</td>
<td>65 – 85</td>
</tr>
<tr>
<td>HHV, MJ/kg</td>
<td>13.9</td>
<td>12.5 – 15.5</td>
</tr>
<tr>
<td>C, wt% d.s.</td>
<td>33.9</td>
<td>30 – 40</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
<td>3.2 – 4.0</td>
</tr>
<tr>
<td>O</td>
<td>35.8</td>
<td>34 – 38</td>
</tr>
<tr>
<td>Na</td>
<td>19.6</td>
<td>17 – 22</td>
</tr>
<tr>
<td>S</td>
<td>4.6</td>
<td>3.6 – 5.6</td>
</tr>
<tr>
<td>K</td>
<td>2.0</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Cl</td>
<td>0.5</td>
<td>0.1 – 4</td>
</tr>
</tbody>
</table>
Molten salts in the recovery boiler

- 200-450°C
- 500-800°C
- 800-1000°C
- 1000-1300°C

Deposition (Na₂SO₄,KCl)

Corrosion

Smelt bed

Smelt: Na₂S+Na₂CO₃
Na₂CO₃ + Na₂S
Equilibria with Molten Phases: Black Liquor Recovery Boiler and Alkali Salts


- Equilibrium modeling of furnace gas and smelt bed of a kraft recovery boiler
- Non-ideal interactions for liquid $\text{Na}_2\text{CO}_3$-$\text{Na}_2\text{S}$ optimized by Gunnar
Thermodynamic databases for alkali salts

Thermodynamic properties of alkali salts
- Na-K-S-C-O-Cl-H system re-evaluated
  - Covers all Na-K components from reducing to oxidizing conditions
  - FTPulp database in Factsage
My PhD defense in 2007
Melting properties of alkali salts & characteristic temperatures

- \( T_0 \), First melting temperature: Corrosion
- \( T_{15} \), Sticky temperature: Deposition
- \( T_{70} \), Flow temperature: Deposit buildup
- \( T_{100} \), Complete melting temperature: Flow properties
Solidus temperature ($T_0$) of superheater deposits from BL recovery boilers

- Solidus measured with DTA
- Deposits contain $\text{Na}^+, \text{K}^+, \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{Cl}^-$
- Thermodynamic model predicts solidus ($T_0$) within $\pm 10^\circ\text{C}$
(Na,K)$_2$SO$_4$ + 1.3% Cl, $T_0=522^\circ$C

Corrosion layer thickness, μm

(Skrifvars et al. 2008)
Liquidus temperatures ($T_{100}$) of $\text{Na}^+, \text{K}^+/\text{Cl}^-, \text{SO}_4^{2-}, \text{CO}_3^{2-}$ mixtures

[Sementsova 1956] [Bergman 1958]
Stickiness of Partially Molten Particles

Entrained Flow Reactor Tests in Toronto

Deposition (mg/g-cm²-min)

Fraction molten phase (wt-%)

(Tran et al. 2002)
Åbo Black Liquor Recovery Boiler Advisor

- **Rainer Backman, Gunnar Eriksson, Kaj Sundström:** The Recovery Boiler Advisor - Combination of Practical Experience and Advanced Thermodynamic Modelling, Proceedings: *3rd Colloquium on Process Simulation*, June 12-14, 1996

- An application of ChemApp on the chemical processes in the kraft recovery boiler

- Windows-based program for boiler designers and operators to predict chemical processes in the furnace and in flue gas channels

- One-dimensional, multi-stage chemistry model using chemical equilibrium calculations, physical models for deposit behavior and experimental information for combustion characteristics
### Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Air Ratio</td>
<td>1.1</td>
</tr>
<tr>
<td>Primary Air Ratio</td>
<td>0.3</td>
</tr>
<tr>
<td>Black Liquor Solids</td>
<td>70.0%</td>
</tr>
<tr>
<td>Precipitator Efficiency</td>
<td>99.0%</td>
</tr>
<tr>
<td>Steam Temperature</td>
<td>473.0°C</td>
</tr>
<tr>
<td>Gas Temperature</td>
<td>850.0°C</td>
</tr>
<tr>
<td>Heat Conductivity</td>
<td>1.030 W/m²K</td>
</tr>
<tr>
<td>Heat Transfer coeff</td>
<td>600.0 W/m²K</td>
</tr>
</tbody>
</table>

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Why thermodynamic modeling is useful for BL combustion

- Well-defined "ash" chemistry (Na-K salts)
- Alkali salts have good contact in smelt bed
- High liquid content in inorganic particles down to 500 °C + molten phase has low viscosity → fast reactions
- Concepts $T_{15}$ and $T_{70}$ work for recovery boilers
Example
Biomass and waste boilers
Major ash-forming elements in different fuels

- Fossil
- Peat
- Wood
- Forest residue
- Bark
- Waste wood
- Agricultural residue

ÅA fuel database
Ash phases

Silicates
- Minerals in fuels
- Polymeric phases
- Ex. KAISi$_3$O$_8$
- High viscosity liquid
- Quasichemical or associate models for thermodynamics

Salt-like phases
- Various formation reactions
- Simple ionic phases
- Examples KCl, CaSO$_4$
- Low viscosity liquid
- Sublattice models for thermodynamics
Fly Ash Composition of *Salix*
Multicomponent Multiphase Thermodynamic Calculation

(Hupa et al. 1999)
Availability of thermodynamic data

Accurate existing data
- Low-alkali silicates (coal, peat)
- Alkali salt mixtures (black liquor)
- Selected Na-K-Ca-Mg-Zn-Pb salt mixtures (on-going) (biomass, waste)

Improvements needed
- K$_2$O-rich silicates (straw)
- Phosphate mixtures (ongoing) (agricultural fuels)
- Unified database for heavy metals
Molten salts
On-going and future developments

- Addition of \textbf{Ca-Mg-Pb-Zn-P} to \textbf{Na-K-S-C-O-Cl-H} system underway to cover all major salt-like phases in biomass and waste combustion
- New approach to include phosphorus in the liquid phase
CaSO$_4$ - (NaCl+KCl)

Liquid contains Ca$^{2+}$, K$^+$, Na$^+$//SO$_4^{2-}$, Cl$^-$
Quaternary reciprocal system
No additional model parameters

Experimental data by Rubleva & Bergman (1956) J. Gen. Chem. USSR
Phosphate chemistry – new results

$\text{K}_2\text{O} - \text{P}_2\text{O}_5$

Liquid

$n(\text{K}_2\text{O})/(n(\text{K}_2\text{O})+n(\text{P}_2\text{O}_5))$

Temperature ($^\circ\text{C}$)
K$_3$PO$_4$-KCl mixture
Model vs experiment

731-733 °C
Example for biomass boilers

Advanced Ash Behaviour Prediction Tool for Biofuel Mixtures

Visual Validation of Deposition Model

Clean

Deposit

Lower part of the right wall

Peat
More of Gunnar’s contributions to combustion applications
Influence of Black Liquor Variability, Combustion, and Gasification Process Variables and Inaccuracies in Thermochemical Data on Equilibrium Modeling Results

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Thermodynamic Modeling of PCDD/Fs Formation in Thermal Processes

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Thermodynamic Behavior of Metal Chlorides and Sulfates under the Conditions of Incineration Furnaces

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Thermodynamic modeling of ash chemistry in combustion

- Useful tool for modeling alkali salt melting and reactions in BL recovery boilers
  - Bed behavior, corrosion, deposit formation
- Useful tool for predicting ash chemistry in biomass and coal combustion
  - Well-defined databases for coal ashes and slags
  - Database for salt phases including Ca, Mg, Pb, Zn, and P is being developed
  - Databases for alkali-rich silicates need development
  - Limitations of kinetics, fuel speciation, combustion techniques need to be addressed for proper use of thermodynamic modeling
Gratulerar Gunnar

önskar
alla vänner vid
Åbo Akademi