Numerical Modeling of the Drying, Devolatilization and Char Conversion Processes of Black Liquor Droplets

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This presentation is based on the Academic dissertation of Mika Järvinen* and its appendix papers done in co-operation with Ron Zevenhoven, Helsinki University of Technology, Mikael Forssen, Åbo Akademi University and Esa Vakkilainen, Jaakko Pöyry Oy.

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1. Motivation and objectives of the work
2. Description of the detailed physical model developed
3. Experimental validation
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5. Contribution of the work and conclusions
Motivation for this work

• Previously developed model was available
  • IPST; Walsh, Horton et al.
  • HUT; Manninen and Vakkilainen
• Improved mass and heat transfer inside BL droplet
• Improved biomass combustion model could be done
Modelling drying

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O} \]

• new expression for BPR
• when does inside of droplet “freeze”
• what causes swelling
• is inside “bubbly”
• what is the surface like

Modelling pyrolysis

\[ \text{P} \rightarrow \text{CH}_n\text{O}_6(s), \text{CO}, \text{CH}_4, \text{C}_2\text{H}_2, \text{Na}, \text{M}_2\text{S}(s) \]
\[ \text{M}_2\text{SO}_4(s), \text{M}_2\text{CO}_3(s), \text{N}_2, \text{NH}_3, \ldots \]

Three models tried
• Kobayashi type two reaction model
• Single reaction model
• Heat transfer controlled
### Modelling pyrolysis

\[ P \rightarrow CH_nO_\alpha(s), \ CO, \ CH_4, \ C_2H_2, \ Na, M_2S(s) \]
\[ M_2SO_4(s), \ M_2CO_3(s), \ N_2, \ NH_3, \ ... \]

- need simultaneous particle temperature and mass loss data with a small time resolution
- need reliable sulfur release model

### Char conversion

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C(s) + H_2O \rightarrow CO + H_2 )</td>
<td>Li et al. 1991</td>
</tr>
<tr>
<td>( C(s) + CO_2 \rightarrow 2 \ CO )</td>
<td>Li et al. 1990</td>
</tr>
<tr>
<td>( C(s) + 0.5 \ O_2 \rightarrow CO )</td>
<td>Smith 1982</td>
</tr>
</tbody>
</table>

### Inorganic reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_2CO_3(s) + 2 \ C(s) \rightarrow 2 \ M + 3 \ CO )</td>
<td>Li et al. 1991</td>
</tr>
<tr>
<td>( Na_2SO_4(s) + 2 \ C(s) \rightarrow Na_2S(s) + 2 \ CO_2 )</td>
<td>Wåg et al., 1995</td>
</tr>
<tr>
<td>( M_2S(s) + 2 \ O_2 \rightarrow M_2SO_4(s) )</td>
<td>Smith 1982</td>
</tr>
</tbody>
</table>
Gas reactions

For CH$_4$ oxidation inside the particle, model of Jones and Lindsted was implemented.

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \text{Fuel breakdown} \]
\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad " \]
\[ \text{H}_2 + 0.5\text{O}_2 \leftrightarrow \text{H}_2\text{O} \quad \text{Oxidation of H}_2 \]
\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \text{CO water shift reaction} \]

Parameters and models extracted from comparison with experiments

- The effective thermal conductivity and pyrolysis heat were obtained
- External flame model in convective conditions

\[ \lambda_e = \lambda_s (1 - \phi^{2/3}) + \frac{\phi^{5/3}}{1 - \phi^{2/3}} + \frac{16\sigma T^3}{3a_r\phi} \]
\[ a_r = 850 \text{ 1/m} \]
Numerical solution

- As the conservation equations and source terms are very complex, a numerical implicit 2nd order method was used
- Solutions of $T(r,t)$, $p(r,t)$, $c_{g.i}(r,t)$, $c_{s.i}(r,t)$

Model validation

- Validation is a very essential part of the model development
- Valuable co-operation with Åbo Akademi; Mikael Forssén et al.,
  - Pyrolysis swelling and size reduction during char conversion
  - New method for measuring swelling and on-line release of species, excellent data for model validation, Forssén (2001)
Swelling and shrinking

- Particle volume increases linearly as pyrolysis proceeds
- When local char conversion reaches value $X_{cr} = 0.8$, cell is removed and particle size decreased

![Graph showing swelling and shrinking](image)

Surface temperatures

- Model was compared with temperature measurement data from Frederick et al. 1994

![Graph showing surface temperatures](image)
Pyrolysis mass and carbon residues

10 sec, 2 mm particle, experiments by Frederick et al.

Carbon release rate

• Thermal conductivity affects on internal temperature distribution
• Model was compared with new ÅA reactor data (2001), sensitivity analysis with respect to effective thermal conductivity and pyrolysis heat was done
• Internal thermal radiation is important
SAMPLE RESULTS FROM THE DETAILED MODEL

Intraparticle temperature and reaction profiles during pyrolysis

Corresponding char reaction profiles during pyrolysis,
Char combustion

Intraparticle temperature and reaction profiles during char combustion

Corresponding inorganic reaction profiles during char combustion

Combustion in flight

Detailed single particle model was implemented into a flight path calculation procedure to solve the interactions of gas velocity and heat and mass transfer rates

- 95% dried
- 95% pyrolyzed
- end of char combustion

0.5, 1 and 2 mm particle trajectories
New char conversion mechanism, Auto-gasification

- $\text{H}_2\text{O}$ and $\text{CO}_2$ flow out from the particle and gasify the hot char surface
- 30-40% char conversion during pyrolysis IN AN INERT ENVIRONMENT
- Direct char oxidation during pyrolysis

Detailed single particle combustion model

- One essential result of the work is the detailed model developed itself (robust, general numerical solution of the conservation equations in porous media)
- Can be applied for other fuels, for studying general heat and mass transfer problems etc.
Main conclusions

- Black liquor particle combustion is a non-isothermal process, combustion stages overlap
- In order to develop a proper CFD sub-model, all the relevant mechanisms need to be understood and considered, experimental validation is a very important part of the model development
- Experimental data can be transferred to furnace conditions by modeling, furnace conditions are very difficult to consider in small scale reactor

DETAILED MODEL - NOT FOR CFD

- Very complex, calculation times up to ~ 60 min, large amount of variables to be stored
- Not possible to use in CFD calculations
- By using this model, relevant mechanisms can be isolated and a proper guidelines for developing a simplified model can be obtained
- When the results from this model are validated with proper experimental data, CDF-submodel can be developed in solid basis
Acknowledgements

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