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

Mika Järvinen and Esa Vakkilainen

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.

* mika.jarvinen@hut.fi, tel: +358 9 451 3657
CONTENTS

1. Motivation and objectives of the work
2. Description of the detailed physical model developed
3. Experimental validation
4. Sample results
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
CHALLENGES IN MODELING THE COMBUSTION OF A SINGLE BLACK LIQUOR PARTICLE
Modelling drying

H$_2$O(l) $\rightarrow$ H$_2$O

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

\[ P \rightarrow CH_{n}O_{o}(s), CO, CH_{4}, C_{2}H_{2}, Na, M_{2}S(s) \]
\[ M_{2}SO_{4}(s), M_{2}CO_{3}(s), N_{2}, NH_{3}, \ldots \]

Three models tried

- Kobayashi type two reaction model
- Single reaction model
- Heat transfer controlled
Modelling pyrolysis

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

• need simultaneous particle temperature and mass loss data with a small time resolution

• need reliable sulfur release model
Char conversion

C(s) + H₂O → CO + H₂  
Li et al. 1991

C(s) + CO₂ → 2 CO  
Li et al. 1990

C(s) + 0.5 O₂ → CO  
Smith 1982

Inorganic reactions

M₂CO₃(s) + 2 C(s) → 2 M + 3 CO  
Li et al. 1991

Na₂SO₄(s) + 2 C(s) → Na₂S(s) + 2 CO₂  
Wåg et al., 1995

M₂S(s) + 2 O₂ → M₂SO₄(s)  
Smith 1982
Gas reactions

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

\[
\begin{align*}
CH_4 + H_2O & \rightarrow CO + 3 H_2 & \text{Fuel breakdown} \\
CH_4 + O_2 & \rightarrow CO + 2 H_2 & \text{"} \\
H_2 + 0.5 O_2 & \leftrightarrow H_2O & \text{Oxidation of H}_2 \\
CO + H_2O & \leftrightarrow CO_2 + H_2 & \text{CO water shift reaction}
\end{align*}
\]
Parameters and models extracted from comparison with experiments

- The effective thermal conductivity and pyrolysis heat were obtained

\[ \lambda_e = \lambda_s (1 - \phi^{\frac{2}{3}}) + \frac{\phi^{\frac{2}{3}}}{1 - \phi^{\frac{1}{3}}} + \frac{16\sigma T^3}{3a_R} \phi \]

\[ a_R = 850 \text{ } \text{l/m}\]

- External flame model in convective conditions
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.

900 °C, 9 mg particle 20 % H$_2$O, 4 % CO, rest N$_2$

Experiments, Frederick et al. 1990
Surface temperatures

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

Carbon release rate for 2.5 mm particle burned in 900 °C, 3 % O₂.
SAMPLE RESULTS FROM THE DETAILED MODEL
Pyrolysis

0.5 mm

Intraparticle temperature and reaction profiles during **pyrolysis**

2 mm

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 needs 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
DETAILLED 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, CFD-submodel can be developed in solid basis
Acknowledgements

This work is a part of the Finnish Modelling Tools for Combustion Process Development (CODE) Program.

The Technology Development Agency of Finland (Tekes), Andritz Corporation, Academy of Finland and Walter Ahlström foundation are acknowledged for financing this work.