Modeling of a strongly coupled Thermal, Hydraulic and Chemical problem:
drying and low-temperature pyrolysis of chromated copper arsenate (CCA)-wood waste particles in a moving bed reactor

Ir. Joan Govaerts
Prof. Dr. Ir. Lieve Helsen
Outline

- Introduction
- Description of the mathematical model
- Simulation results
- Conclusions
CCA-impregnated wood

- CCA stands for Chromated Copper Arsenate
- Preserves wood from insects, fungi and water damage
- Decks, fences, utility poles, playground equipment…
CCA-impregnated wood

- Since 1970, phase-out in 2005
- Nowadays restricted to a limited number of industrial applications
- Classified as hazardous waste
- Service life of 10–40 years: disposal will continue long into the future
- Worldwide problem (U.S.: peak disposal rate of 9.7 million m³ wastewood in 2008)
- Need for a sustainable disposal method
Low T - carbonisation

- Promising technology
  - < 370°C
  - Wood chips are converted to carbon and volatile organic compounds: energy recuperation
- Material recuperation:
  - Heavy metals remain in solid phase
  - Carbon product
- Low tar production/emission

- Simulation model
  - Influence of operational parameters
  - Optimal working conditions
  - Controlling metal and tar emissions
Description of the mathematical model

- Model assumptions
- Governing equations
- Submodels
- Initial and boundary conditions
- Numerical Solution
Model assumptions

- Volume Averaging – continuum approach
- 1D anisotropic porous medium
- reaction products are lumped into three main groups: char, tar and volatiles
- Only As-Oxide considered
  - Cu, Cr very stable
  - bound, condensed, gaseous
- Water: bound, vapor
- Solid and gas phase at different T
- No secondary reactions (low T)
  - Cracking of tars
  - Secondary char formation
Governing equations

- **Continuity gas phase**
  \[
  \frac{\partial \tilde{\rho}_g}{\partial t} + \nabla \cdot \left( \tilde{\rho}_g \tilde{\nabla} \tilde{\mathbf{v}} \right) = \tilde{S}_g
  \]

- **Darcy Law**
  \[
  \tilde{\mathbf{v}} = -\frac{\kappa}{\mu} \nabla \tilde{p}_g
  \]

- **Species conservation**
  \[
  \frac{\partial \tilde{\rho}_s}{\partial t} \tilde{Y}_k + \nabla \cdot \left( \tilde{\rho}_s \tilde{Y}_k \tilde{\nabla} \tilde{\mathbf{v}} \right) = \nabla \cdot \left( D_s \nabla \tilde{Y}_k \right) + \tilde{S}_k
  \]
  \[
  \frac{\partial \tilde{\rho}_s}{\partial t} \tilde{Y}_k + \nabla \cdot \left( \tilde{\rho}_s \tilde{Y}_k \tilde{\mathbf{v}} \right) = \tilde{S}_k
  \]
Governing equations

- **Energy conservation**

\[
\frac{\partial \varepsilon_g}{\partial t} + \nabla \cdot \left( \rho_g c_{p,g} T_g \mathbf{v} \right) = \nabla \cdot \left( D_{th} \left( \nabla T_g \right) \right) - \frac{A_{gs}}{V_g} h_{sg} \left( T_g - T_s \right) + \mathbf{S}^g_{th}
\]

\[
\frac{\partial \varepsilon_s}{\partial t} + \nabla \cdot \left( \rho_s c_{p,s} T_s \mathbf{v} \right) = \nabla \cdot \left( k_{s,eff} \left( \nabla T_s \right) \right) - \frac{A_{gs}}{V_g} h_{sg} \left( T_s - T_g \right) + \mathbf{S}^s_{th}
\]

with \( \rho_s = \sum \rho_w Y_k \)
Submodels

- Drag force; heat and mass dispersion
  - Darcy coefficients
  - Dispersion tensor
    - Experimentally determined (Govaerts & Mayerhofer, 2010)
- Convective heat transfer
  \[ h_{sg} = \xi k_g (2 + 1.1 Pr^{1/3} Re^{0.6}) / d_p \]  (Wakao & Kugei, 1982)
- Solid conductivity
  \[ k_{s,eff} = (1 - \varepsilon_g) \left( d_p h_{rs} + \frac{k_g}{\Psi} \right) \]  (Yagi & Kunii, 1957)

\[ h_{rs} = 0.227 \frac{\varepsilon}{2 - \varepsilon} \left( \frac{T_{s}}{100} \right)^3 \]
Submodels

- **Thermal degradation of wood**
  \[
  \begin{align*}
  &\text{wood} \rightarrow \text{volatiles} \quad (k_1) \\
  &\text{wood} \rightarrow \text{tar} \quad (k_2) \quad k_i = A_i \exp\left(\frac{E_i}{RT}\right) \\
  &\text{wood} \rightarrow \text{char} \quad (k_3)
  \end{align*}
  \]

- No secondary reactions
  (cracking/secondary char formation)
As-release
- first order single reaction scheme with an Arrhenius temperature dependency.
- $A = 6.5 \times 10^{-3} \text{ s}^{-1}$ and $E_a = 20.4 \text{ kJ/mol.}$ (Helsen and Van den Bulck, 2000)
- As-release is restricted to range of 280°C-450°C

As-condensation/re-evaporation: diffusion-limited

$$m_{As} = \frac{A_{gs}}{V_g} k_m (p_{As, sat} - p_{As})$$

with $k_m = D_g \left(2 + 1.1 \text{Sc}^{1/3} \text{Re}^{0.6}\right) / d_p$
Submodels

- Drying/condensation: diffusion-limited

\[
m_{As} = \frac{A_{gs}}{V_g} k_m (p_{H_2O, sat} - p_{H_2O})
\]

with \( k_m = D_g (2 + 1.1Sc^{1/3} Re^{0.6}) / d_p \)

- To avoid over- and undershoots Heaviside functions are used
Latest additions:
As-release/condensation

- As-release is restricted to range of 280°C-450°C
- As-condensation/re-evaporation: diffusion-limited

\[ m_{As} = \frac{A_{gs}}{V_g} k_m (p_{As,sat} - p_{As}) \]

with \[ k_m = D_g (2 + 1.1Sc^{1/3} Re^{0.6}) / d_p \]
Boundary and initial conditions

- **Initial conditions**
  - Ambient temperature, pressure
  - \( V_g = 0 \)

- **Boundary conditions**
  - Inlet: \( T_g = 370^\circ C, V_g = V_{in} \)
  - Outlet: \( P = P_{atm}; \, \text{gradients}=0; \, V_{solid} \)
Numerical solution

- Solve gas & solid species conservation equation
- Update physico-chemical properties
- Solve gas & solid species conservation equation
- Update physico-chemical properties
- Solve Darcy & Energy equations

Outer iteration

Time iteration

START

t = t + ∆t

Update physico-chemical properties

Convergence?

no

yes

Convergence?

no

yes

STOP
Simulation Results

- Objectives
  - Maximise wood conversion and char production
  - Minimise tar- and As-emission
  - Short hot zone
  - Long cold zone
Simulation Results

- drying efficiency of about 100%
- wood conversion of 99.4 %,
  - 29.9% charcoal
  - 22.1% volatiles
  - 47.4% tars
- No condensation of tar and secondary char formation
  - tar emissions are probably overestimated
  - the overall product efficiency of the process underestimated.

- Relative mass and energy balance errors
  - 0.029 %
  - -0.077 %
Simulation Results

Axial temperature profile at nominal flow rates

![Axial temperature profile graph](image_url)
Simulation Results
Axial As-oxide concentrations at nominal flow rates

- 13.2 % of the initial As is released due to thermal decomposition
- 12.9 % of the initial As-content will leave the reactor as a volatile compound.
- 0.3% gets condensed in the middle part of the reactor.
- adsorption/desorption, formation of stable metal-mineral compounds not considered
Conclusions

- model for the simulation of the thermochemical decomposition of CCA-wood in a packed bed reactor.
  - unsteady, one-dimensional conservation equations of heat and mass for the solid and the gas phase,
  - Darcy’s law
  - a competitive reaction mechanism for wood decomposition
  - drying
  - arsenic oxide release/condensation.
- This model allows to investigate the influence of design parameters (e.g. the volumetric flow rate of the hot gas supplied at the bottom and wood residence time)
  - product distribution
  - As-release
  - temperature profiles