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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

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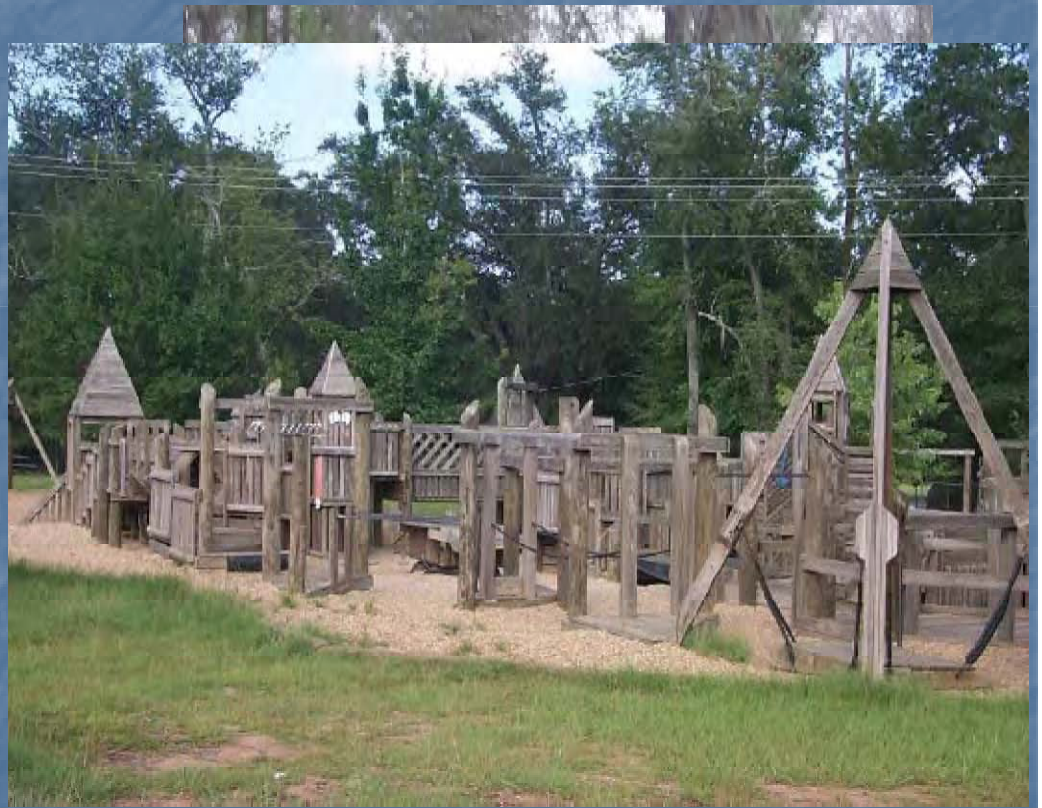
Outline

- Introduction
- Description of the mathematical model
- Simulation results
- Conclusions

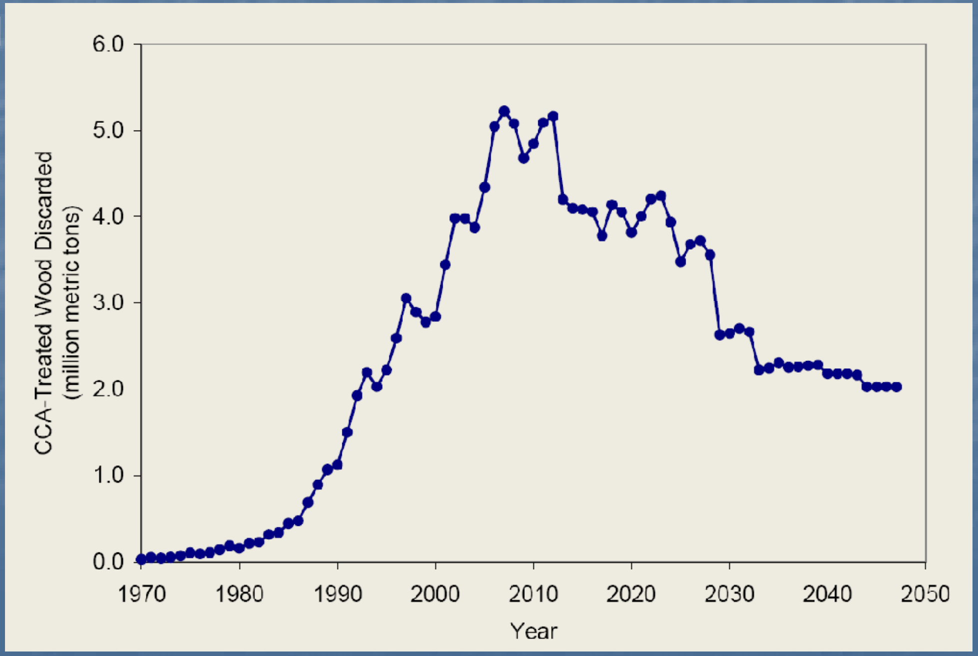
CCA-impregnated wood

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



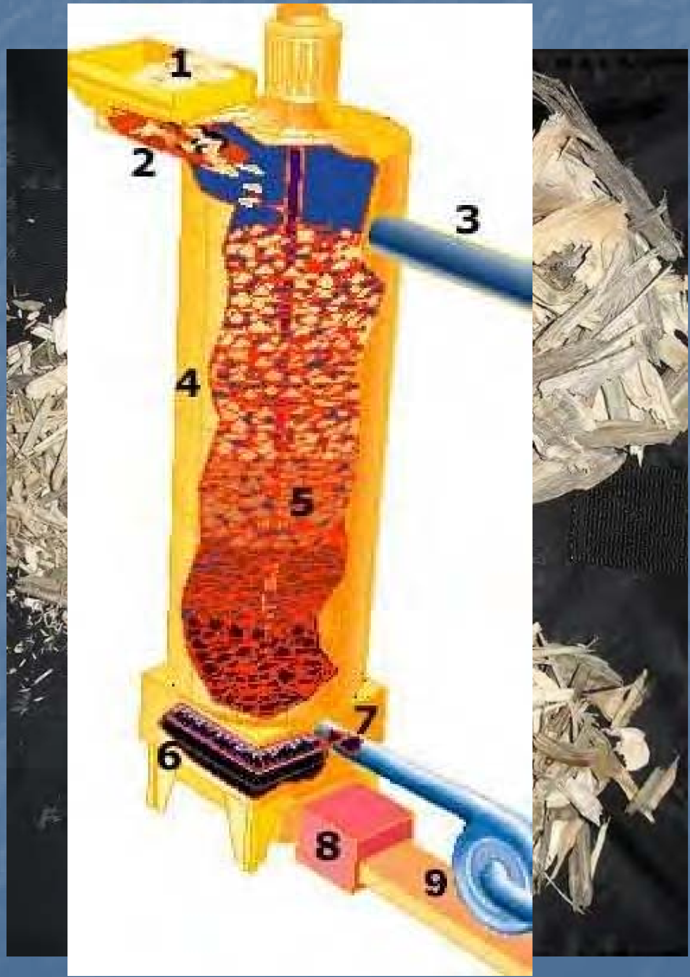
CCA-impregnated wood

- 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 su



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

$$\frac{\partial \varepsilon_g \widetilde{\rho_g}^g}{\partial t} + \nabla \cdot \left(\varepsilon_g \widetilde{\rho_g}^g \tilde{v} \right) = S_g$$

- Darcy Law

$$\tilde{v} = -\frac{\kappa}{\mu} \nabla \tilde{p}^g$$

- Species conservation

$$\frac{\partial \varepsilon_g \widetilde{\rho_g}^g \widetilde{Y_k}^g}{\partial t} + \nabla \cdot \left(\widetilde{\rho_g}^g \widetilde{Y_k}^g \tilde{v} \right) = \nabla \cdot \left(\mathrm{D}_g \nabla \cdot \widetilde{Y_k}^g \right) + \widetilde{S_k}^g$$

$$\frac{\partial \varepsilon_s \widetilde{\rho_s}^s \widetilde{Y_k}^s}{\partial t} + \nabla \cdot \left(\widetilde{\rho_s}^s \widetilde{Y_k}^s V_s \right) = \widetilde{S_k}^s$$

Governing equations

- Energy conservation

$$\frac{\partial \varepsilon_g \widetilde{\rho_g}^g \widetilde{c_{p,g}}^g \widetilde{T_g}^g}{\partial t} + \nabla \cdot \left(\widetilde{\rho_g}^g \widetilde{c_{p,g}}^g \widetilde{T_g}^g \tilde{v} \right) = \nabla \cdot \left(\mathrm{D}_{th} \left(\nabla \cdot \widetilde{T_g}^g \right) \right) - \frac{A_{gs}}{V_g} h_{sg} \left(\widetilde{T_g}^g - \widetilde{T_s}^s \right) + \tilde{S}^g{}_{th}$$

$$\frac{\partial \varepsilon_s \widetilde{\rho_s}^s \widetilde{c_{p,s}}^s \widetilde{T_s}^s}{\partial t} + \nabla \cdot \left(\widetilde{\rho_s}^s \widetilde{c_{p,s}}^s \widetilde{T_s}^s V_s \right) = \nabla \cdot \left(k_{s,eff} \left(\nabla \cdot \widetilde{T_s}^s \right) \right) - \frac{A_{gs}}{V_g} h_{sg} \left(\widetilde{T_s}^s - \widetilde{T_g}^g \right) + \tilde{S}^s{}_{th}$$

with $\widetilde{\rho_s}^s = \sum \widetilde{\rho_w}^s \widetilde{Y_k}^s$

Submodels

- Drag force; heat and mass dispersion
  - Darcy coefficients
  - Dispersion tensor

  → Experimentally determined (Govaerts & Mayerhofer, 2010)
- Convective heat transfer

  $h_{sg} = \xi k_g (2 + 1.1 \mathrm{Pr}^{1/3}\, \mathrm{Re}^{0.6}) / d_p$ (Wakao & Kugei, 1982)
- Solid conductivity

$$k_{s,eff} = (1 - \varepsilon_g)\left(d_p h_{rs} + \frac{k_g}{\Psi} \right) \quad \text{(Yagi \& Kunii, 1957)}$$

$$\text{with } h_{rs} = 0.227 \frac{\varepsilon}{2 - \varepsilon} \left(\frac{T_s^{s}}{100} \right)^3$$

Submodels

- Thermal degradation of wood

$$\begin{cases} wood \rightarrow volatiles & (k_1) \\ wood \rightarrow tar & (k_2) \\ wood \rightarrow char & (k_3) \end{cases} \qquad k_i = A_i \exp(E_i / RT)$$

- No secondary reactions (cracking/secondary char formation)

Submodels

- As-release
  - first order single reaction scheme with a Arrhenius temperature dependency.
  - A = 6.5 × 10-3 s^{-1} and E_a = 20.4 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

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

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

Submodels

- Drying/condensation: diffusion-limited

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

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

- To avoid over-and undershoots Heaviside functions are used

Latest addittions: As-release/condensation

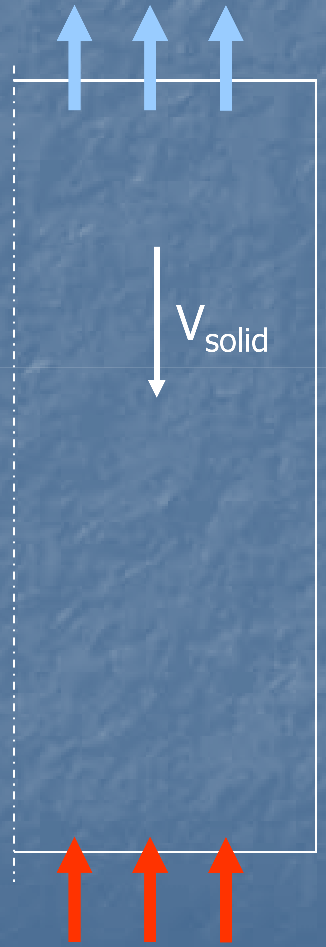
- As-release is restricted to range of 280°C-450°C
- As-condensation/re-evaporation: diffusion-limited

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

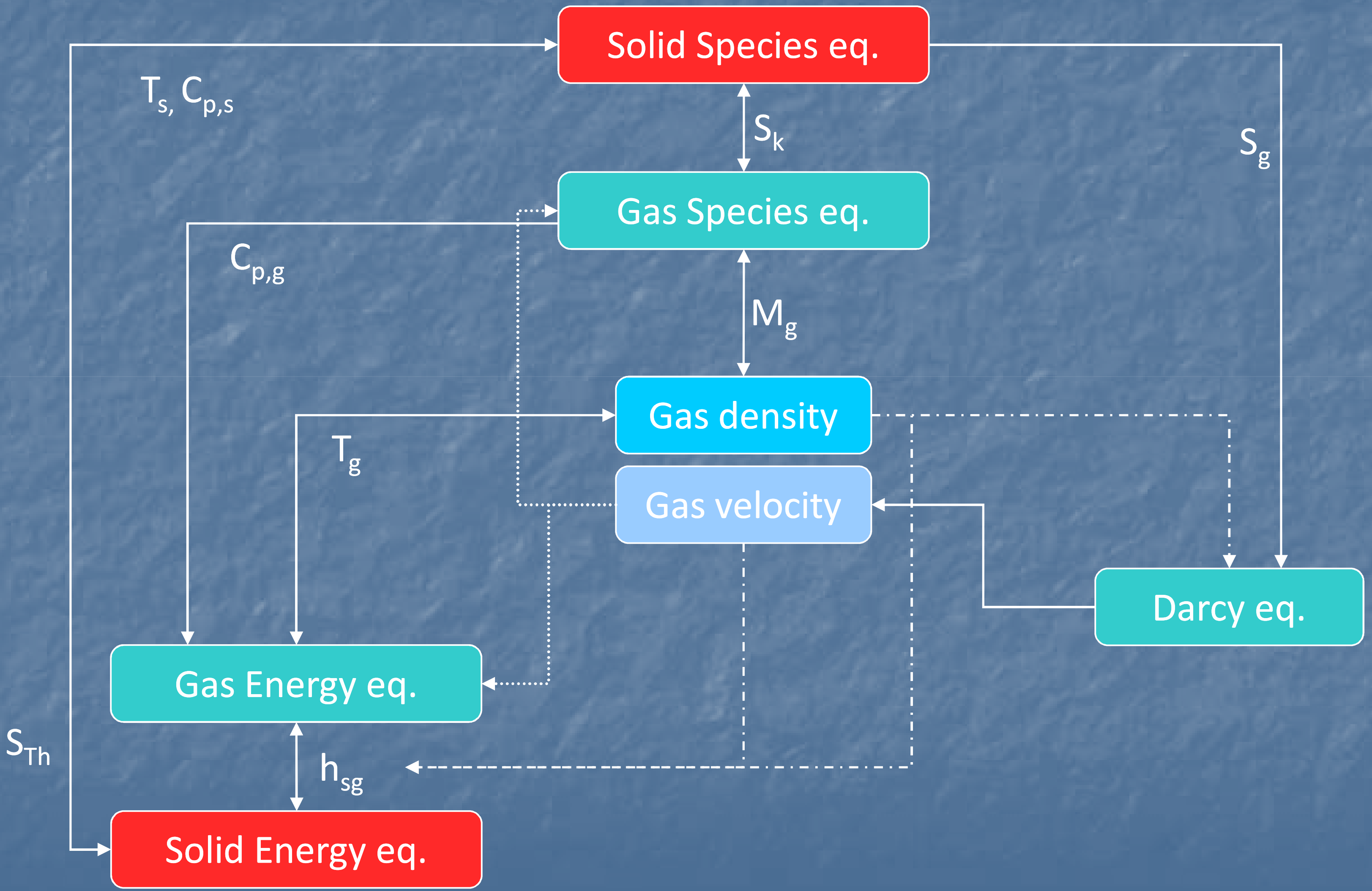
$$\text{with } k_m = D_g (2 + 1.1 \mathrm{Sc}^{1/3} \mathrm{Re}^{0.6}) / d_p$$

Boundary and initial conditions

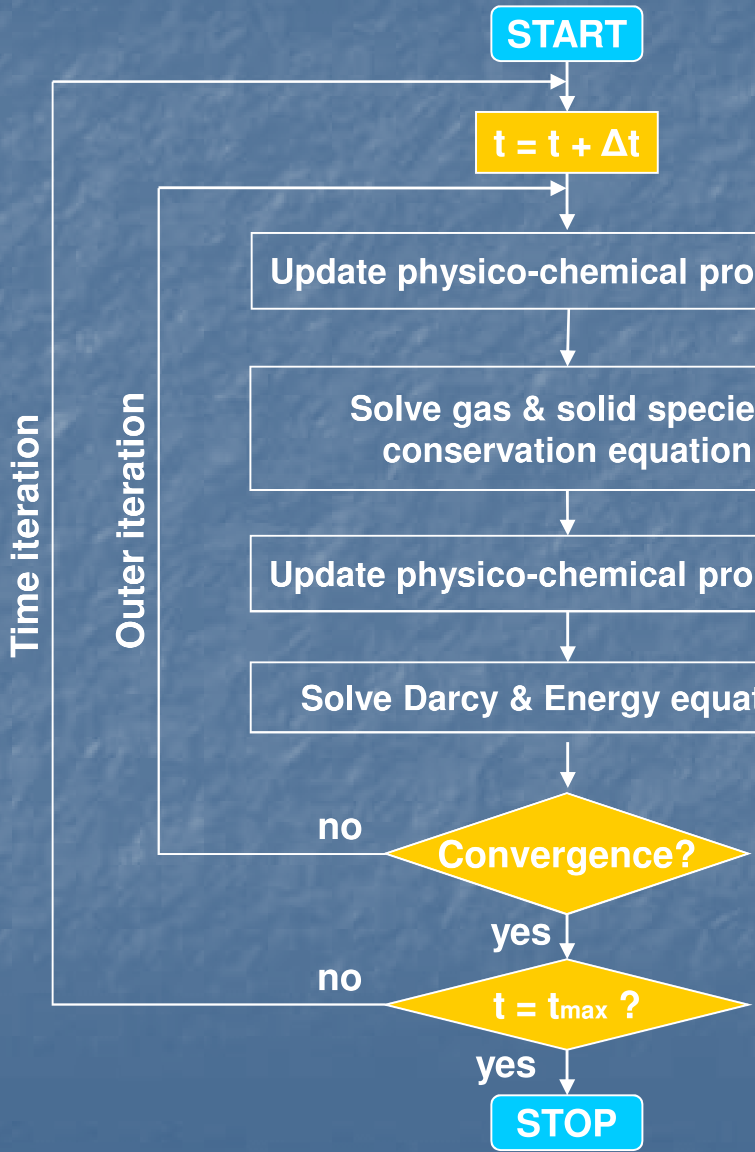
- Initial conditions
  - Ambient temperature, pressure
  - $V_g = 0$
- Boundary conditions
  - Inlet: T_g=370°C, $V_g=V_{in}$
  - Outlet: $P=P_{atm}$; gradients=0; V_{solid}



Couplings


Solid Species eq.
$T_{s}, C_{p,s}$
S_k
S_g
Gas Species eq.
$C_{p,g}$
M_g
Gas density
T_g
Gas velocity
Darcy eq.
Gas Energy eq.
S_{Th}
h_{sg}
Solid Energy eq.

Numerical solution



Simulation Results

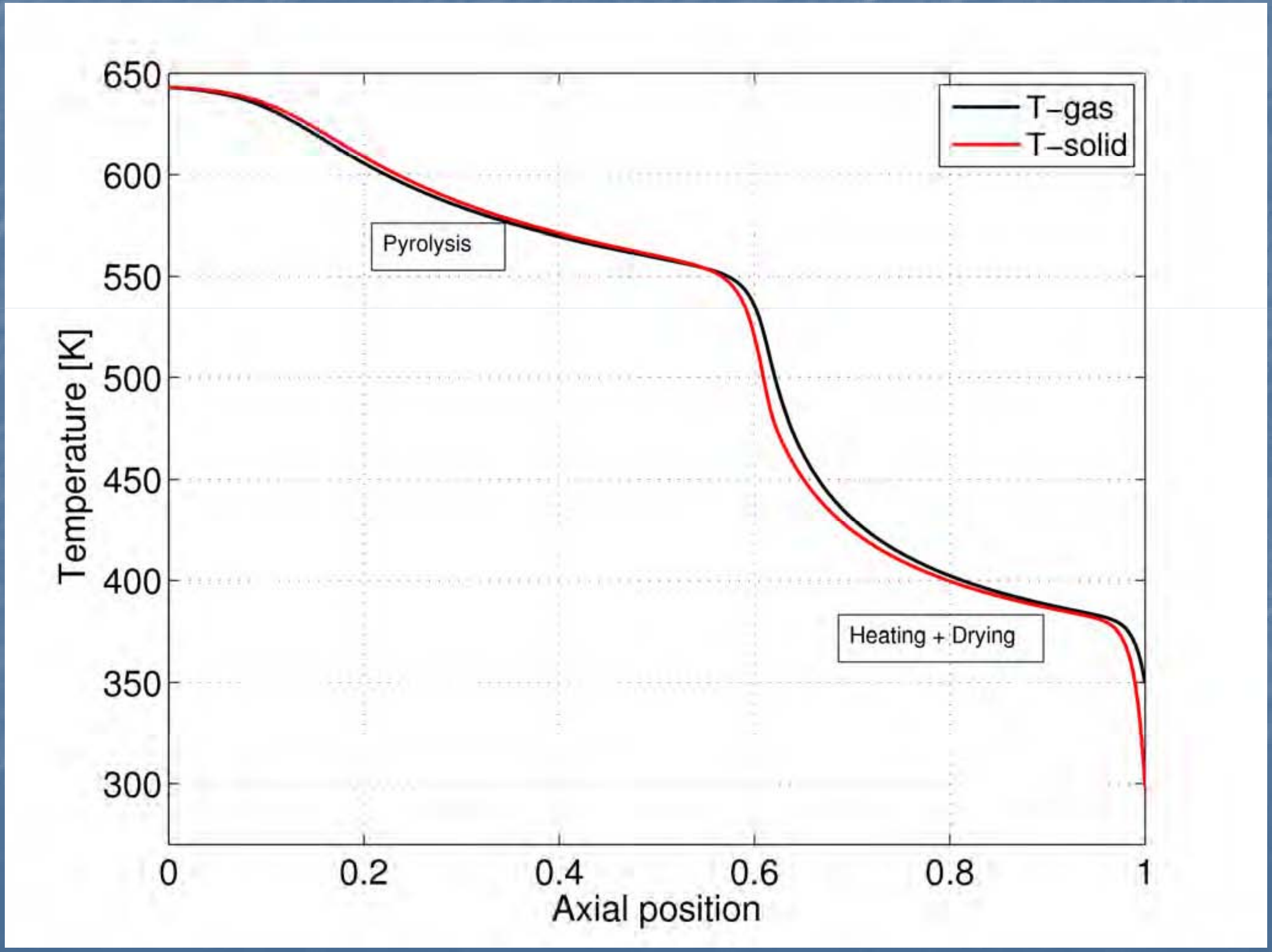
- Objectives
  - Maximise wood conversion and char production
  - Minimise tar- and As-emission
  - Short hot zone
  - Long cold zone

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 %

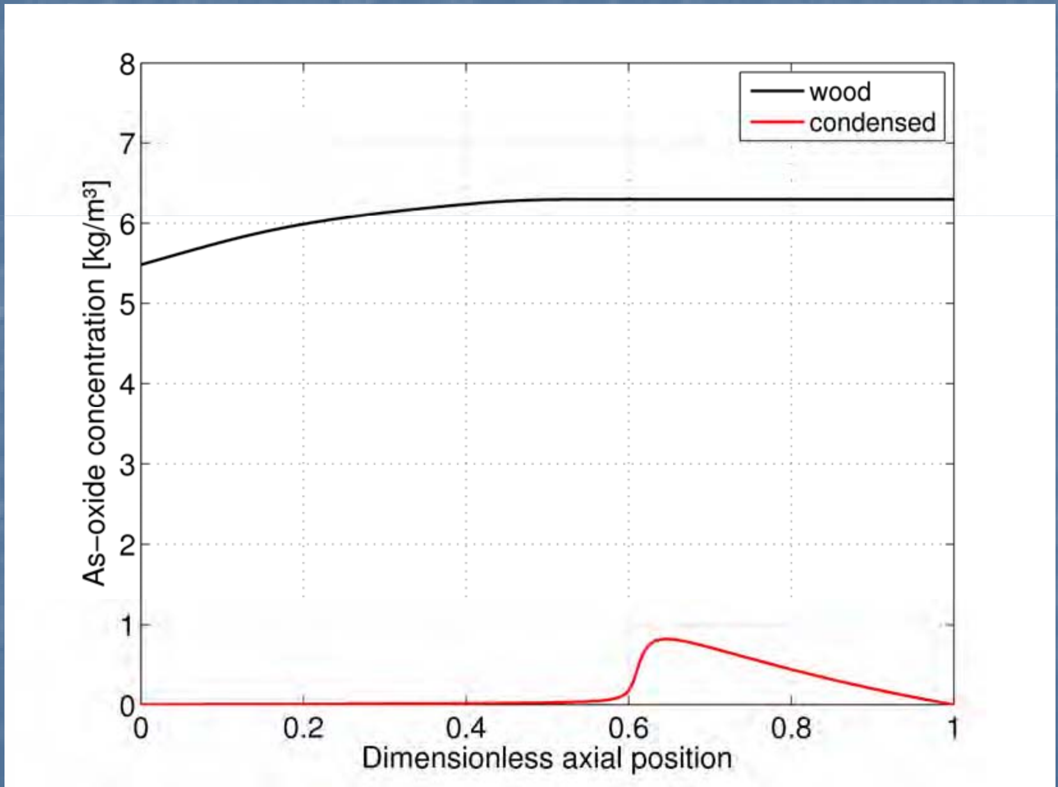
Simulation Results

Axial temperature profile at nominal flow rates



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