

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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Abstract: Low temperature thermal carbonization might be the ultimate solution to the growing disposal problem of chromated copper arsenate (CCA) - treated waste wood. This energy and material recuperating technology is currently in the process of upscaling to an industrial level. In the present study, a numerical reactor model is developed in COMSOL multiphysics that allows to investigate the temperature profiles, gas velocity, char and combustible gas yields and emissions of tars and arsenic during the thermal carbonization of CCA-wood in a moving bed reactor. Strong couplings exist between all equations due to the source terms, changes in gas density/velocity and other physical properties. The resulting system becomes very stiff and recourse has to be made to an iterative, sequential solving procedure to obtain the steady state solution making use of a MATLAB code.

Keywords: CCA Impregnated wood, pyrolysis, reactor modeling

Introduction

Thermal carbonization seems to be a promising technology for material and energy recuperation starting from wood waste [1]. One of the main concerns related to thermal treatment of CCA impregnated wood waste is the production of tars and the release of volatile toxic metal species. Tars (a complex mixture of organics like acids, phenols, cresols and PAH's) are, besides the fact that some components are highly toxic, harmful for combustion engines due to corrosion and fouling [2, 3].

The thermochemical process considered in this study aims at minimizing these emissions by combining a low-temperature slow pyrolysis (carbonization) with a distillation-like process.

During the process the crushed wood, introduced at the top of the reactor, is heated in a reaction column by subjecting it to a flow of hot gas (85% nitrogen and 15 % water) which enters at the bottom. The wood is carbonized, releasing volatile combustible vapors (light gases and tars) and producing a coal-type residue that entraps the agglomerated metals and minerals. The agglomerates of metals and minerals can be removed from the carbon product by a centrifugal separation of the solid residue, hereby concentrating the heavy metals for recycling or disposal.

The combustible vapors are washed in a water scrubber and subsequently burnt in a gas burner that supplies energy to the system. The wood at the bottom of the column is subjected to a well defined elevated pressure and temperature, transforming it to a coal-type product. The pressure as well as the temperature decreases stepwise with the height of the wood column. The vapors, released by thermal decomposition of the wood, flow upward where part of them is condensed due to the cooling effect of the wood column. These condensed compounds are cracked or recombined when they arrive again in the hot zone at the bottom of the column, and so on. The process is thus characterized by a sequence of evaporation, cooling, condensation, heating, cracking, where the wood column acts both as a condenser and as a filter [4, 5].

To obtain a more profound insight into the processes that occur in the reactor and the way they can be controlled, a new simulation model has been developed that enables the study of the influence of the most important operational parameters. The model presented in this paper consists of the unsteady, one-dimensional continuity equation for the gas phase, Darcy equation, the solid and gas phase species

conservation equations and two-temperature enthalpy conservation equations. Furthermore, models for the arsenic release and condensation are incorporated in the simulation model. The coupling of these models delivers an interesting tool that can be used for control purposes which is highly innovative.

Description of the model

The reactor consists of decomposing wood particles with gas flowing through the inter-particle void space. The packed bed is treated as a continuous porous medium which moves downwards along the reactor axis at a constant speed. This allows application of a volume-averaged form of the macroscopic conservation equations [6]. The wood particles are considered as rectangles with a constant volume and are assumed to be thermally thin, which means that intra-particle temperature differences are neglected [7]. Past studies have shown that for temperatures below 600°C the impact of shrinkage on predictions of the pyrolysis yield is negligible and, as such, shrinkage can also be ignored in the model [8].

The following volume averaged conservation equations are derived by carrying out an averaging process using so-called *Representative Elementary Volumes* (REV) [9]

Darcy equation

$$\tilde{v} = -\frac{\kappa}{\mu} \nabla \tilde{p}^g \quad (1)$$

Gas phase continuity

$$\frac{\partial \varepsilon_g \tilde{\rho}_g^g}{\partial t} + \nabla \cdot (\tilde{\rho}_g^g \tilde{v}) = S_g \quad (2)$$

Gas Species conservation

$$\frac{\partial \varepsilon_g \tilde{\rho}_g^g \tilde{Y}_k^g}{\partial t} + \nabla \cdot (\tilde{\rho}_g^g \tilde{Y}_k^g \tilde{v}) = \nabla \cdot (\mathbf{D}_g \nabla \cdot \tilde{Y}_k^g) + \tilde{S}_k^g \quad (3)$$

Solid Species conservation

$$\frac{\partial \varepsilon_s \tilde{\rho}_w^s \tilde{Y}_k^s}{\partial t} + \nabla \cdot (\tilde{\rho}_w^s \tilde{Y}_k^s V_s) = \tilde{S}_k^s \quad (4)$$

Gas and solid phase energy conservation

$$\frac{\partial \varepsilon_g \tilde{\rho}_g^g c_{p,g}^g \tilde{T}_g^g}{\partial t} + \nabla \cdot (\tilde{\rho}_g^g c_{p,g}^g \tilde{T}_g^g \tilde{v}) = \quad (5)$$

$$\nabla \cdot \left(\mathbf{D}_{th} (\nabla \cdot \tilde{T}_g^g) \right) - \frac{A_{gs}}{V_g} h_{sg} (\tilde{T}_g^g - \tilde{T}_s^s) + \tilde{S}_{th}^g$$

$$\frac{\partial \varepsilon_s \tilde{\rho}_s^s c_{p,s}^s \tilde{T}_s^s}{\partial t} + \nabla \cdot (\tilde{\rho}_s^s c_{p,s}^s \tilde{T}_s^s V_s) =$$

$$\nabla \cdot \left(k_{s,eff} (\nabla \cdot \tilde{T}_s^s) \right) - \frac{A_{gs}}{V_g} h_{sg} (\tilde{T}_s^s - \tilde{T}_g^g) + \tilde{S}_{th}^s \quad (6)$$

$$\text{with } \tilde{\rho}_s^s = \sum \tilde{\rho}_w^s \tilde{Y}_k^s$$

In equations (1) - (6) v is the gas velocity [m/s], p [Pa] is the pressure, μ is the fluid dynamic viscosity [Pa·s], κ is the permeability of the porous medium [m²], ε the porosity of the medium, Y_k is the mass fraction of species k , D_g is the dispersion tensor [m²/s] and V_s is the solid velocity [m/s]. S_g and S_k are the production (> 0) or consumption (< 0) rates of the gas phase and species k . The gas mixture is assumed to show an ideal behavior. Five gas phase species are considered: nitrogen gas, volatiles (light combustible gases), tars, water vapour and As₄O₆. The density of the gases are determined from the ideal gas law (IGL):

$$\tilde{\rho}_g^g = \frac{\tilde{p}^g M_g}{R \tilde{T}_g^g} \quad (7)$$

with M_g the molecular weight and R the universal gas constant (8.31 J K⁻¹mol⁻¹). The molecular weights of the volatiles and tars are not easily determined since they consist of a large number of components. In accordance with the work of Grönli [10], the molecular weight of benzene (0.110 kg/mol) has been chosen to represent the tars while an average value between carbonmonoxide and carbondioxide (0.038 kg/mol) has been assumed for the volatiles. In the solid phase, three species are considered (wood, char, moisture and As₂O₃). T_g and T_s are respectively the gas temperature and the solid temperature [K], $c_{p,g}$ and $c_{p,s}$ are respectively the gas specific heat [J/(kg·K)] and the solid specific heat, D_{th} is the thermal dispersion tensor [W/(K·m)], A_{gs} is the area of the solid-gas interface, h_{sg} is the convective heat transfer coefficient between the solid surface and the gas [W/(m²K)], V_s is the solid velocity (the solid is moving downward) [m/s], $k_{s,eff}$ is an effective conductivity for the solid particles and S_{th} is the energy released (> 0) or consumed (< 0) by the

chemical reactions in the gas and solid phase. The energy conservation equations for the gas and solid phase are based on two-temperatures models, for which the averaging procedure is well explained by others [11-13].

Assuming that the Lewis number ($Le = \frac{\alpha}{D}$ where α is the thermal diffusivity and D is the molecular diffusivity) of the flow is equal to one, so that the mass dispersion and heat dispersion are equivalent, the dispersion tensors can be modeled as proposed by Mal *et al.* [14] :

$$D_g = \widetilde{\rho}_g^g D \text{ and } D_{th} = \widetilde{\rho}_g^g \widetilde{c}_{p,g}^g D \quad (8)$$

with $D = L: \begin{matrix} \widetilde{v} \\ \widetilde{v} \\ \widetilde{v} \\ \widetilde{v} \end{matrix}$

L is a fourth order tensor of which coefficients depend on the geometric characteristics of the porous bed. The wood bed is assumed to be an orthotropic porous medium. The dispersion coefficients have been experimentally determined using tracer gas injection and FID measurements on a column of rectangular wood chips by Tilmans and Jeanmart [15].

The convective heat and mass transfer coefficients are modeled using the correlations proposed by Wakao and Kaguei [16].

$$h_{sg} = \xi k_g (2 + 1.1 \text{Pr}^{1/3} \text{Re}^{0.6}) / d_p \quad (9)$$

$$k_m = D(2 + 1.1 \text{Sc}^{1/3} \text{Re}^{0.6}) / d_p \quad (10)$$

$$\text{where } \text{Re} = \varepsilon_g \widetilde{v}^g d_p \rho_g / \mu, \quad \text{Pr} = \frac{c_{p,g} \mu}{k_g},$$

$\text{Sc} = \frac{\mu}{\rho_g D}$, d_p is the equivalent diameter of the particle and k_g is the gas conductivity. ξ , taken as 0.10, [17] accounts for the effect of heterogeneous reactions on the gas-to-solid heat transfer. Consequently the convective heat transfer coefficient is kept within the range of 5 - 30 W / m².K, commonly observed in static bed pyrolyzers [18].

The correlation for the effective conductivity in a packed bed can be obtained from the studies of Yagi and Kunii [19] and Kunii and Smith [20]. Based on correlations and physical considerations for the relevant modes of heat transfer in the solid phase of the bed (radiation

between adjacent particles and conduction through the stagnant film of fluid surrounding contact points between particles), this effective solid conductivity can be expressed as:

$$k_{s,eff} = (1 - \varepsilon_g) \left(d_p h_{rs} + \frac{k_g}{\Psi} \right) \quad (11)$$

where Ψ is a parameter relating the diameter d_p to the equivalent length for conduction at contact points, and h_{rs} is the coefficient of heat transfer by radiation between solid surfaces. The value of Ψ can be found in Kunii and Smith [20] as a function of the ratio between solid and gas conductivities and the type of packing, and the value of h_{rs} is given by the equation:

$$h_{rs} = 0.227 \frac{e}{2 - e} \left(\frac{\widetilde{T}_s^s}{100} \right)^3 \quad (12)$$

where e is the emissivity of the solid.

Moisture evaporation and condensation is represented as a diffusion limited process [21] where the rate of the process is determined by the difference between the partial gas pressure of water vapour and the saturation vapour pressure calculated by the Clausius-Capeyron expression. Heaviside smoothing functions are used to avoid over-and undershoots of moisture and water vapour concentrations due to this formulation of the evaporation/condensation process.

$$S_m = \frac{A_{gs}}{V_g} k_m \left(\rho_{sat,H_2O} - \widetilde{\rho}_{H_2O}^s \right) \quad (13)$$

To simulate the thermochemical decomposition of CCA wood a competitive reaction model is used (see Figure 1 **Error! Reference source not found.**). The virgin fuel is considered as a homogeneous single species which undergoes thermal degradation. Pyrolysis reaction products are lumped into three main groups: char, tar and volatiles. Secondary reactions of tar are not taken into account due to the low reactor temperatures applied (below 400°C) [18].

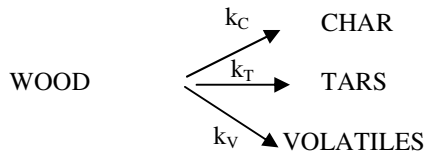


Figure 1: Competitive reactions scheme for thermochemical decomposition of wood

A large variety of kinetic constants exists in the literature. Di Blasi [18] stated that kinetic models with lower activation energies are more suited for predicting the behavior of chemical reactors in practical applications. Since the kinetic data from Di Blasi and Branca [22] perform best in reproducing the experimental trends of char and gas production in low-temperature pyrolysis, these are chosen. The kinetic parameters are listed in Table 1.

Arsenic is identified as the problematic compound regarding metal release. In freshly treated wood arsenic is fixed in pentavalent state, but in weathered wood arsenic may be partly reduced to the trivalent state.

The precise mechanism of As-release is not yet entirely known. It is generally accepted though, that arsenic compounds are first reduced to As_2O_3 upon heating, after which it is gasified according to the equilibrium $2As_2O_3 \leftrightarrow As_4O_6$ with As_4O_6 being the dominant species for temperatures up to $1073^\circ C$ [23, 24]. A chemical scheme, modeling this arsenic release is incorporated in the simulation model. This model was developed by Helsen and Van den Bulck [25] and predicts the arsenic release according to a first order single reaction scheme assuming an Arrhenius temperature dependency. The rate frequency factor and activation energy are: $A = 2.48 s^{-1}$ and $E_a = 53.6 kJ/mol$.

This simple model succeeds well in describing the As-release of lab-scale and thermogravimetric experiments with CCA-impregnated wood for the temperature range of $300 - 450^\circ C$. It is assumed that no As-release occurs below $280^\circ C$, which is implemented using a smoothing function between 280 and $300^\circ C$. The initial As-content is set to $1.05 wt\%$, which is higher than the levels found in CCA-treated wood waste, to simulate a worst-case scenario.

Once the As_4O_6 is released from the wood, the evaporation and condensation of this volatile

compound is taken into account with an diffusion limited model similar to water evaporation/condensation. The remaining parameters, input data or correlations that are needed for the simulation are listed in Table 1.

Table 1: Input variables and correlations

<i>Kinetic parameters</i>	<i>wood</i>	<i>degradation:</i>
$k = A \exp(-E/RT)$ with $E(kJ/mol)$, $A (s^{-1})$ [22]		
$k_C = 3.3 \times 10^6 \exp(-112/RT)$		
$k_V = 4.4 \times 10^9 \exp(-153/RT)$		
$k_T = 1.1 \times 10^{10} \exp(-148/RT)$		
$\Delta H = 4180 kJ/kg$		
<i>Porosity</i> $\epsilon_g = 0.54$ [15]		
<i>Density of wood</i> $\rho_w = 600 kg/m^3$ [15]		
<i>Initial water content</i> $15 wt\%$		
<i>Dynamic viscosity gas</i> $\mu = 3 \times 10^{-5} kg/ms$ [26]		
<i>Diffusivity gas</i> $D = 2 \times 10^{-5} m^2/s$		
<i>Heat conductivity gas</i> $k_g = 0.0515 W/mK$ [15]		
<i>Inlet gas temperature</i> $T_{g,inlet} = 370^\circ C$		
<i>Heat capacity of the individual species (kJ/kgK) as a function of temperature [T][10]</i>		
<i>Volatiles</i> $c_{pv} = 0.77 + 6.29 \times 10^{-4}T - 1.91 \times 10^{-7}T^2$		
<i>Tar</i> $c_{pt} = -0.10 + 4.40 \times 10^{-3}T - 1.57 \times 10^{-6}T^2$		
<i>Nitrogen</i> $c_{pn} = 975.6 \times 10^{-3} + 0.2223 \times 10^{-3}T - 3.394 \times 10^{-8}T^2$		
<i>Wood</i> $c_{pw} = 1.5 + 1 \times 10^{-3}T$		
<i>Char</i> $c_{pc} = 0.42 + 2.09 \times 10^{-3}T - 6.85 \times 10^{-7}T^2$		

Use of COMSOL Multiphysics

For numerical model implementation equations from the Earth science and Chemical engineering modules are used. Dirichlet boundary conditions are imposed at the inlet and zero gradient boundary conditions at the outlet. The exit pressure is kept at ambient value. Strong couplings exist between all equations due to the source terms, changes in gas density/velocity and other physical properties (see Figure 2), the resulting system becomes very stiff and recourse has to be made to an iterative, sequential solving procedure to obtain the steady state solution. Therefore a Matlab code has been written which solves the set of equations in three blocks. Firstly, the solid and gas species equations are solved simultaneously. Secondly the Darcy and energy equations are solved. These two blocks of equations are iteratively solved until convergence. Finally, using this converged solution as a starting point, the adaptive mesh refinement solver is used to obtain a grid-independent solution.

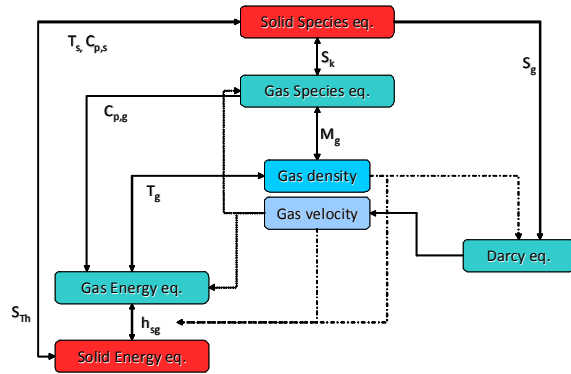


Figure 2: Couplings between the different equations

Results and discussion

In this section simulation results are presented. In order to check the accuracy of the numerical solution for the reactor model the relative errors in the mass and energy balances are calculated. A correct mass and energy balance assures that the physical quantities mass and energy are conserved in the simulation domain when all processes are accounted for. A separate module was programmed in MATLAB which calculates the in- and outgoing mass and energy fluxes of both phases. The mass balance error, for instance, is calculated as follows:

$$\text{mass balance error}[\%] = \frac{\text{flux}_{in}^{\text{wood}} + \text{flux}_{in}^{\text{mixture}} + \text{flux}_{in}^{\text{heating_gas}} - \text{flux}_{out}^{\text{wood}} - \text{flux}_{out}^{\text{char}} - \text{flux}_{out}^{\text{mixture}} - \text{flux}_{out}^{\text{pyrolysis_gas}}}{\text{flux}_{in}^{\text{wood}} + \text{flux}_{in}^{\text{mixture}} + \text{flux}_{in}^{\text{heating_gas}}} \cdot 100 \quad (14)$$

One calculation is performed at the nominal gas and wood flow rate. Relative mass and energy balance errors are respectively 0.029 % and -0.077 %, which is very satisfactory given the complex system characterized by gas generation and phase changes. At the nominal gas flow rate the process will reach a drying efficiency of about 100% and a wood conversion of 99.4 %, which corresponds to the production of 29.9% charcoal, 22.1% volatiles and 47.4% tars. As the condensation of tar and secondary char formation from the tar compounds are not taken into account, tar emissions are probably overestimated and the overall product efficiency of the process will be underestimated. Temperature profiles of the solid and the gas phase are shown in Figure 3 Two distinct zones

are present: a heating/drying zone and a pyrolysis zone. One can notice the solid temperature rising above the gas temperature due to the conversion of wood to charcoal in the pyrolysis zone. As charcoal has a lower specific heat compared to wood, the solid phase temperature will have to rise to ensure energy conservation.

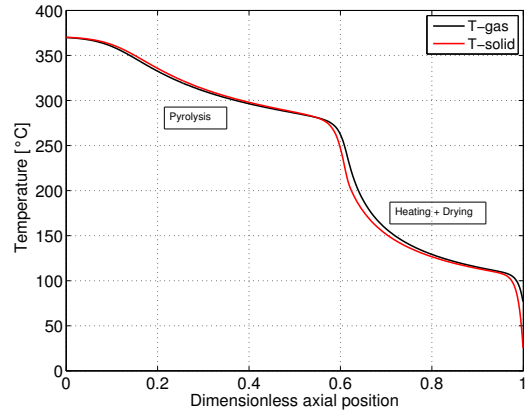


Figure 3: Temperature profiles in the reactor at the nominal gas and wood flow rates

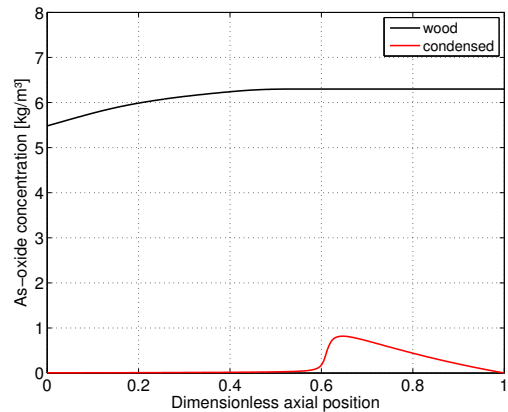


Figure 4: Profiles of As-oxide concentrations in wood and condensed phase at the nominal gas and wood flow rates

The arsenic oxide concentrations as a wood-bounded compound and a condensed compound are shown in Figure 4. About 13.2 % of the As is released from the wood due to thermal decomposition and volatilisation and 12.9 % of the initial As-content will leave the reactor as a volatile compound. The difference is explained by the condensation of As-oxide in the middle part of the reactor. It is expected that physical

processes such as adsorption/desorption, formation of stable metal-mineral compounds, elevated pressures, ... highly influence (and reduce) the ultimate arsenic release. Further (experimental) research is carried out to incorporate these effects in the arsenic behavior model.

Conclusion

This paper presents a model for the simulation of the thermochemical decomposition of CCA-wood in a packed bed reactor. The model includes the 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 and a kinetic model for arsenic release. First results are presented for nominal conditions. 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) on product distribution, metal release and temperature profiles.

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