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Modelling and simulation of porous, reactive particles in liquids: delignification of wood

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Abstract

A mathematical model including coupled chemical reactions and diffusion limitations in anisotropic wood chips was derived. A numerical algorithm that combines finite difference methods and backward difference methods was used as an efficient method to solve the mass balances of wood chips in batch reactors. The numerical strategy and the software can be used to predict the progress of industrial delignification, i.e. production of cellulose.

Keywords: delignification, wood, mathematical model, kinetics

1. Introduction and background

Paper is one of the most important materials used by the mankind. The origin of paper is in wood, which consists of cellulose, hemicelluloses, lignin and extractives. A big part of paper production is based on chemical pulping, which implies that lignin (a complex macromolecular substance), extractives and most part of hemicelluloses are removed from the wood material in order to get cellulose, which is used for paper production. In chemical pulping, the wood chips are brought into contact with a cooking liqueur, which typically consists of alkali (NaOH) and hydrogen sulphide (Sjöström 1989).

The chemical reactions in pulping are numerous, but the overall process can be described as

Lignin+Cellulos+ Carbonhydrates+Xylane+OH+HS-> Dissolved components (1)

In spite that mathematical modeling and simulation of reactive solids is a well-studied topic in chemical engineering (e.g. Salmi et al. 2003), both for gas-solid reactions (e.g. in combustion) and some liquid-solid reactions (e.g. in metallurgy), quantitative modelling of wood delignification has obtained very little attention (Christensen et al. 1983, Gustafson et al. 1983, Andersson 2003). Many of the models presented in literature are extremely empirical by their character, and are not based on real mass and energy balances for the wood material. Furthermore, real chemical compounds are not used in the description of the reaction kinetics and diffusion effects are incorporated in a pseudo-kinetic approach. The evident reason for the very simplified treatment is the challenge of the problem: the chemical system is very complex, involving hundreds of reactions, which are difficult to identify in detail; the wood material undergoes

structural changes during the delignification, the wood material is anisotropic and the process is heavily time-dependent, dynamic by its character.

2. Model for a wood chip

In the present contribution, we introduce a general quantitative description for delignification of anisotropic wood chips under dynamic conditions and present suitable numerical algorithms for model solution. A model including coupled chemical reactions and diffusion limitations in a wood chip is considered. A mass balance for a wood chips is set up by considering a volume element.

Our model is based on the following fundamental hypotheses: an arbitrary number of (pseudo)components and chemical reactions can be included, the wood material is porous and anisotropic, the mass transport inside the wood chips proceeds via diffusion – typically the concept of an effective diffusion coefficient is utilized – but the diffusion flux changes because of changes in the chemical composition and because of structural changes of the wood chips during the delignification. Furthermore, delignification is a highly time-dependent process; thus the model is fully dynamic. Based on these assumptions, the mass balance for the wood chip can initially expressed by

$$\begin{aligned}&\left(N_{ix}A_{yz}\right)_{\text{in}}+\left(N_{iy}A_{xz}\right)_{\text{in}}+\left(N_{iz}A_{xy}\right)_{\text{in}}+r_i'\Delta V=\\&\left(N_{ix}A_{yz}\right)_{out}+\left(N_{iy}A_{xz}\right)_{out}+\left(N_{iz}A_{xy}\right)_{out}+\frac{dn_i}{dt}\end{aligned}\tag{2}$$

where (N_i A) denote the fluxes to or from the wood chip. The volume of a wood chip with the dimensions Δx, Δy and Δz is $\Delta V=\Delta x\Delta y\Delta z$ and the molar amount is obtained from $n_i=\left(\varepsilon_p\Delta V\right)c_i=c_i\varepsilon_p\Delta x\Delta y\Delta z$

The notations introduced are inserted in the original balance equation and the volume element is let to shrink. We obtain a differential equation

$$\frac{d\left(\varepsilon_p c_i\right)}{dt}=-\frac{dN_{ix}}{dx}-\frac{dN_{ix}}{dx}-\frac{dN_{ix}}{dx}+r_i\tag{3}$$

The further treatment of the balance equations depends on the model for diffusion. The simplest approach is based on the use of effective diffusion coefficient, i.e.

$$N_{ix}=-De_{ix}\frac{dc_i}{dx}\tag{4}$$

The effective diffusion coefficient is obtained from $D_{ei}=\varepsilon_p/\tau_p\ D_i$ where the porosity-to-tortuosity ratio is denoted by $\varepsilon_p/\tau_p=\varepsilon'$, $De_{ix}=e'_xD_i$ etc. The model can thus be rewritten to

$$\frac{d\left(\varepsilon_p c_i\right)}{dt}=D_i\left(\varepsilon_x'\frac{d^2c_i}{dx^2}+\varepsilon_y'\frac{d^2c_i}{dy^2}+\varepsilon_z'\frac{d^2c_i}{dz^2}\right)+r_i'\tag{5}$$

The structural parameters (ε_p, ε'_x, ε'_y and ε'_z) change during the delignification process.

The boundary conditions are listed as follows: the concentrations outside the wood chip are locally known ($c_i=c_{Li}$ at $x=Lx$, $y=Ly$, and $z=Lz$, where Lx, Ly and Lz denote the total length of the chip in various directions) and the concentration gradients vanish at the centre of the chip ($dc_i/dx=dc_i/dy=dc_i/dz=0$ at $x=y=z=0$). In the next stage, the chip model is included in an appropriate reactor model. The initial conditions are given as known ones, i.e. ci(x,y,z) at t=0 is known.

3. Reactor model

Here the simplest possible reactor model, namely a completely backmixed batch reactor is considered. The reactor is loaded with the cooking chemicals (e.g. sodium hydroxide or sodium sulphide), the chips are merged into the liqueur at a low temperature, at which the reaction rates are still negligible. The temperature is increased rapidly to the reaction temperature. Thus uniform concentration profiles are assumed in the beginning of the reaction.

We assume firstly a uniform particle distribution and only one particle (chip) in the reactor. A mass balance for a batch reactor containing wood chips becomes

$$N_{ix}A_{yz} + N_{iy}A_{xz} + N_{iz}A_{xy} + r_i V_L = \frac{dn_{Li}}{dt} \tag{6}$$

The notations $n_{li}=c_{Li}\varepsilon_L V=c_{Li}V_L$ are introduced. If the liquid volume is $V_L \approx$ constant then $A_{yx}/V_L=a_{yz}$ etc.

$$N_{ix}a_{yz}V_L + N_{iy}a_{xz}V_L + N_{iz}a_{xy}V_L + r_i V_L = \frac{dc_{Li}}{dt}V_L \tag{7}$$

and the the final for of the balance equation becomes

$$\frac{dc_{Li}}{dt} = N_{ix}a_{yx} + N_{iy}a_{xz} + N_{iz}a_{xy} + r_i \tag{8}$$

where the fluxes N are defined at the outer surface of the chip,

$$N_{ix} = -\varepsilon_x' D_i \left(\frac{dc_i}{dx}\right)_{x=Lx} \tag{9}$$

The fluxes at the outer surface are obtained from the solution of the balance equation (5) of the porous chip. The initial condition is $c=c(0)$ at $t=0$, i.e. the bulk-phase concentrations are known in the beginning. The model can easily be extended to account for particle size distributions.

4. Structural changes of the wood chip

A crucially important factor is to describe the structural changes of wood chips during delignification. Generally one can state that the porosity of the chip increases during the process, since lignin and hemicelluloses are dissolved (Laatikainen 2003).

The porosity change is modelled with three parameters: the initial porosity (ε_{0p}), the final porosity (ε_∞) as well as a parameter, which describes how the porosity changes with the overall conversion of lignin (η_l). A tractable semi-empirical model can be

achieved by the following reasoning: the porosity change with time is described by an empirical differential equation $d\varepsilon_p/dt = a(\varepsilon_\infty-\varepsilon_p)$which has the analytical solution

$$\varepsilon_p = \varepsilon_\infty - \left(\varepsilon_\infty - \varepsilon_{0p}\right)e^{-\alpha t} \tag{10}$$

On the other hand, the overall conversion of lignin (l) is defined as

$$\eta_l = \frac{c_{0l} - c_l}{c_{0l}} = 1 - \frac{c_l}{c_{0l}} \tag{11}$$

For instance, for a first-order reaction, the time dependence of the conversion in a pseudo-homogeneous batch system is given by ln(1-η)=-kt, where k is the apparent rate constant. After solving the time (t) from this equation and inserting it into the semi-empirical expression (9), we get (a/k=α') get the following equation describing the porosity increase:

$$\epsilon_p = \epsilon_{0p} + \left(\epsilon_\infty - \epsilon_{0p}\right)\left(1 - \left(1 - \eta_l\right)^{\alpha'}\right) \tag{12}$$

The model approaches smoothly $\varepsilon_p=\varepsilon_\infty$ as the conversion (η_l) approaches unity ($\eta_l \rightarrow 1$). Parameter α' describes the form of the porosity curve in a very flexible way. For instance, for α'=1, a linear porosity increase is obtained, for higher α'-values an asymptotic behaviour is obtained. It should be noticed that the semi-empirical expression is by no means limited to (pseudo)first order reactions – the first-order hypothesis was just used to illustrate a logical pathway to expression (11), which can even be taken *ad hoc*, based on experimental evidence.

5. Numerical approach

The model equations were solved numerically by discretizing the partial differential equations (PDEs) with respect to the spatial coordinates (x, y, z). Central finite difference formulae were used to approximate the spatial derivatives in eq. (5). Thus the PDEs were transformed to ordinary differential equations (ODEs) with respect to the reaction time with the use of the powerful finite difference method. The created ODEs were solved with the backward difference method with the software LSODE or LSODES (for sparse systems) (Hindmarsh 1983).

6. Simulation example

As an illustration, the very simplified reaction system eq (1) is considered. The reaction rates for the different wood species can be described with the kinetic expression $r_i=k_l(c_{OH}^{\alpha}\ c_{HS}^{\beta}+k_2)c_i$. (Andersson 2003), according to which lignin, carbohydrates, glucomannanes and xylanes are regarded as separate pseudo-components. The temperature dependence of the rate constants is calculated with the Arrhenius formula.

6.1. Simulation results

The numerical algorithms were implemented in a software running on PC. The total number of ODES to be solved was typically 2550 (for 13 discretization points in the wood chip). Simulation tests showed in an unequivocal way that the ODE solver

LSODES was superior to other ones tried (see section 'Numerical approach'). The main reason is that the system is very sparse to discretization. LSODES can nicely handle sparse systems and some initial testing revealed that the sparse solver LSODES was about 6 times faster than the other solvers.

The simulations run smoothly and revealed the dynamic concentration changes inside the wood chip. Some examples are displayed in the figures (Figs 1 and 2) below. The model, consisting of hundreds of differential equations works both for individual chips and for batch reactors filled with chips. The concentration profiles in the wood chip, the porosity change as well as the Kappa number inside the chip are obtained as simulation results. Changes in temperature and cooking chemical concentrations can also be accounted for by the simulation program.

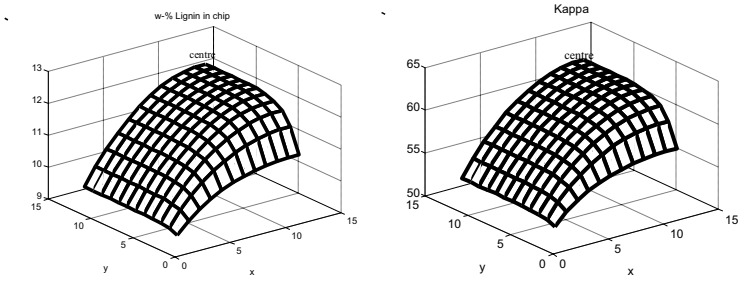

Figure. 1. Concentration (w%) of lignin (left) and Kappa number (right) in wood chip.

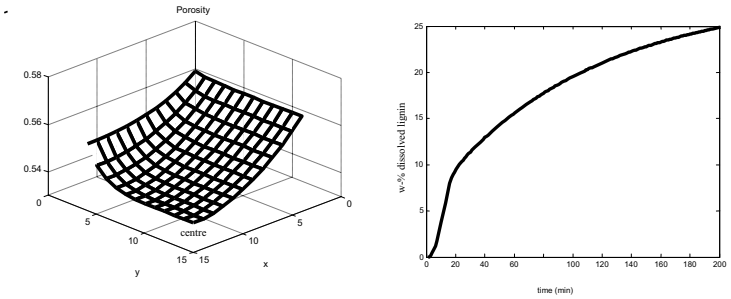

Figure. 2. Porosity in wood chip (left) and concentration of dissolved lignin in bulk phase as a function of time (right).

7. Conclusions

A general dynamic model and software for the description of wood lignification were developed and solved numerically for example cases, which concerned delignification of wood chips in perfectly backmixed batch reactors. Structural changes and anisotropies of wood chips are included in the model. The software utilizes standard stiff ODE solvers combined with a discretization algorithm for parabolic partial differential equations. Example simulations indicated that the selected approach is fruitful, and the software will in future be extended to continuous delignification processes with more complicated flow patterns.

8. Notation

a	surface area-to-volume, m^{-1} , empirical constant, eq. (10), s^{-1}
A	area, m^2
c	concentration, mol/m^3
D, D_e	molecular diffusion coefficient, m^2/s, effective diffusion coefficient, m^2/s
i	component index
k	rate constant, $(m^3/mol)^{n-1}/s$, where n=the reaction order
l	reaction index
n	amount of substance, mol
N	flux, mol/m^2s
p	particle, dimensionless subscript
r	reaction rate, mol/m^3s
r_i, r'_i	component generation rate, mol/m^3s, (r_i, bulk, r' chip)
t	time, min
T	temperature, K
V	volume, m^3
x,y,z	coordinates, m
α,β	empirical exponents in rate expressions, dimensionless
α'	empirical parameter in the porosity model, eq. (12), dimensionless
ε, ε'	porosity, dimensionless, porosity-to-tortuosity ratio, dimensionless
η	conversion, dimensionless
υ	stoichiometric coefficient, dimensionless
τ	tortuosity, dimensionless

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