Mesoscale reaction-diffusion modelling of lignin solvolysis

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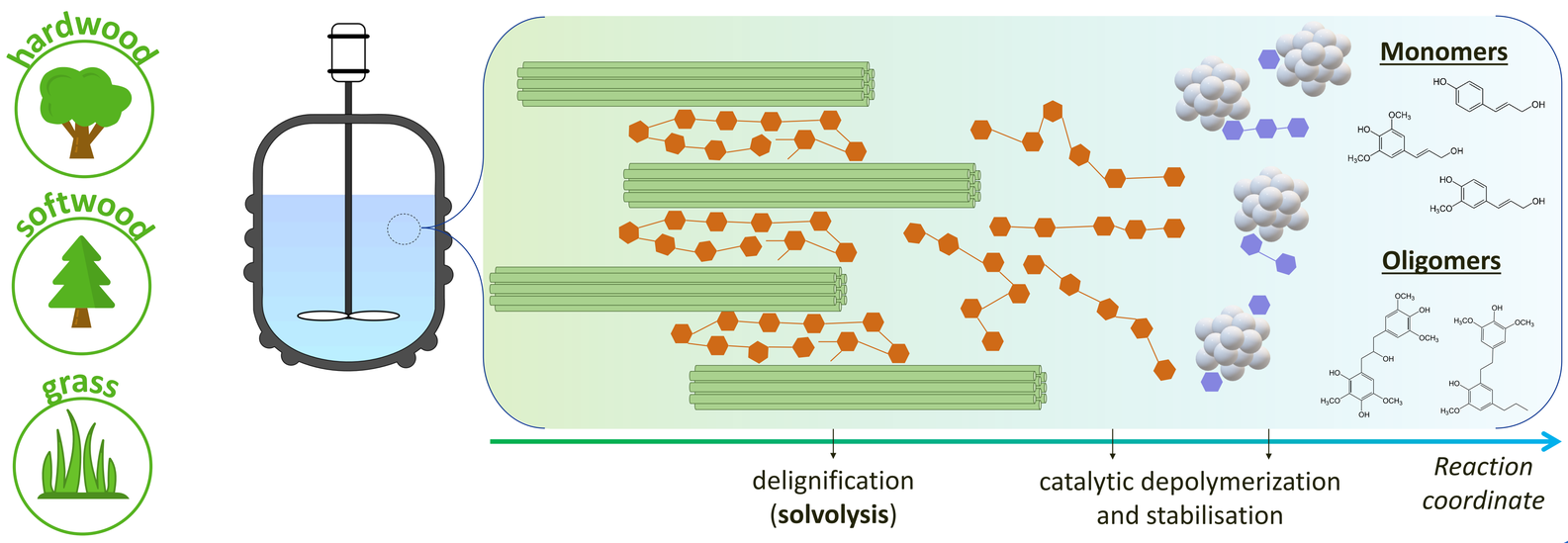
Introduction

- **Lignocellulosic biomass:** alternative feedstock for sustainable manufacturing of chemicals and materials.
- Lignin fraction is the **largest source of renewable aromatics in the planet**.
- The **lignin-first** (*LF*) biorefinery concept complements traditional carbohydrate biorefining, with focus on lignin valorization.
- The reductive catalytic fractionation (RCF) of biomass combines the **solvolytic extraction of the lignin fraction** with catalytic lignin depolymerization and stabilization.
- Key first step for further lignin valorization: determine **intrinsic kinetics of lignin solvolysis**.

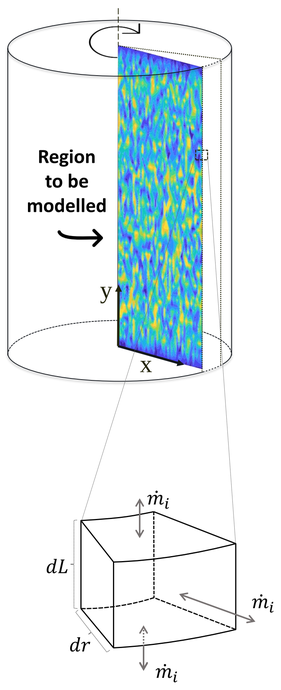
Lignocellulosic feedstocks



Reaction-diffusion model

General considerations

- A biomass pellet of cylindrical shape is assumed;
- (Non)isothermal conditions;
- Pores can be axially-oriented or randomly-oriented;
- Assumption for the lignin fraction: homopolymer characterized by its MW;
- Random distribution of the lignin fraction in the solid domain;
- External transfer coefficients are calculated through correlations.



Model equations

The coupled partial differential equations (PDE's) are solved numerically using an implicit finite difference scheme.

$$\frac{\partial c_i}{\partial t} = D_{eff}(T)\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_i}{\partial r}\right)+\frac{\partial^2 c_i}{\partial z}\right)+r_i \qquad \frac{\partial T}{\partial t} = \alpha(T,\varepsilon_p)\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{\partial^2 T}{\partial z}\right)$$

$$D_{eff}(T) = \frac{\varepsilon_p}{\tau}\boldsymbol{D_{i,CW}(T)}$$

$$-\boldsymbol{k_{0,f}}e^{\frac{-E_{a,f}}{RT}}c_i c_{solv} + \boldsymbol{k_{0,r}}e^{\frac{-E_{a,r}}{RT}}c_{i,sol}$$

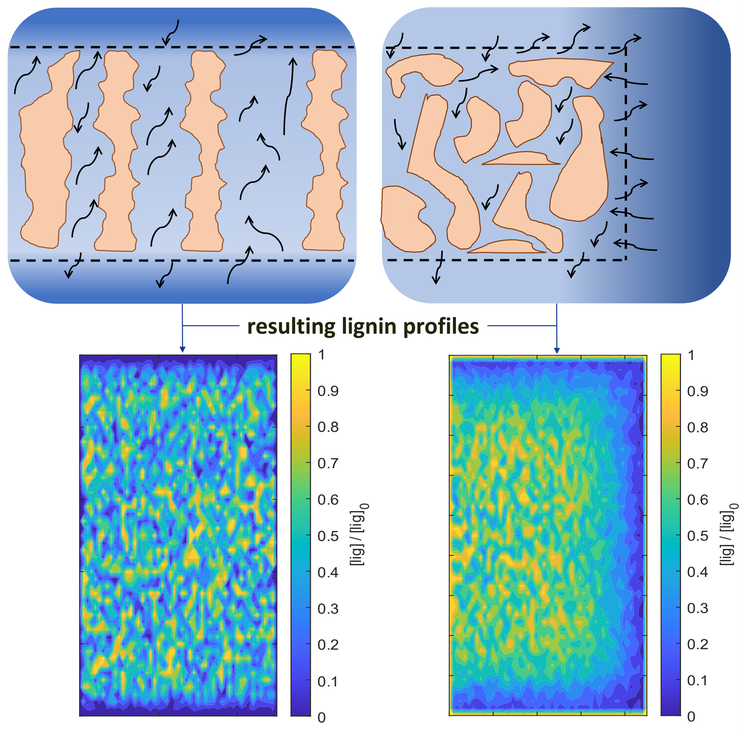
$$D_i(T,MW) = \frac{k_b T}{6\pi\mu_{liq} r_{hyd}}$$

Power law relationships to calculate r_{hyd} ⟶ $r_{hyd}(MW) \propto MW^{\alpha}$ ⟶ *Link between the polymer structure and the solvent environment, e.g. α ≈ 0.5 for ϑ-solvents*

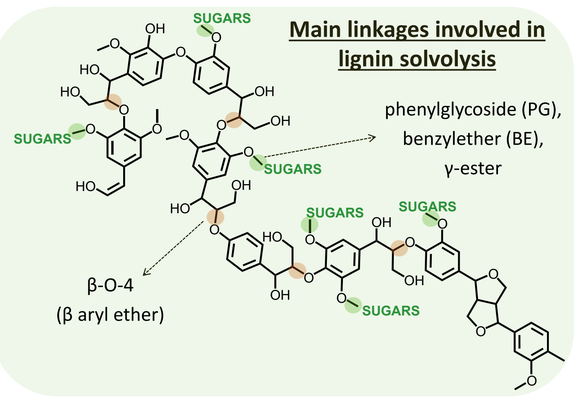
Resistance in series ⟶ $\frac{1}{D_{CW}} = \frac{1}{D_i} + \frac{1}{\frac{d_p}{3}\sqrt{\frac{8RT}{\pi MW_i}}}$ (Knudsen diffusivity)

Diffusion through axially-oriented pores (left) and through randomly-oriented pores (right)

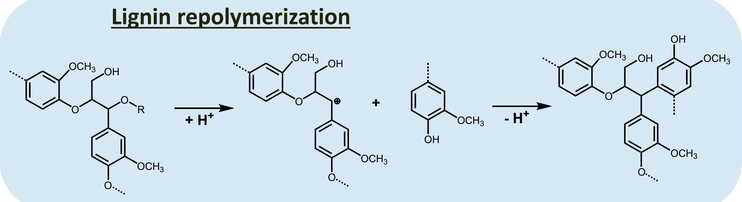
(dashed line: interphase between particle and bulk domain)



Main linkages involved in lignin solvolysis



Lignin repolymerization

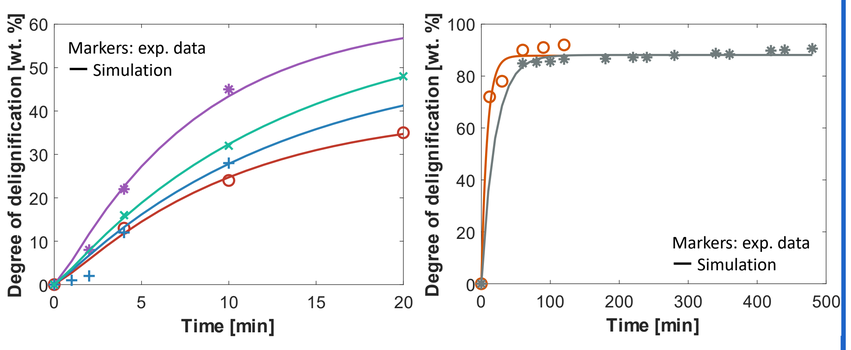


Application

Lignin and temperature profiles

Data fitting using and calculation of the Thiele modulus

(experimental data extracted from literature)



Hardwood (birch) - methanol system

- Size: 0.15mm – 1.50mm (Temp: 220°C)
- Size: 0.12mm – 0.95mm (Temp: 230°C)
- Size: 0.12mm – 0.95mm (Temp: 240°C)
- Size: 0.12mm – 0.95mm (Temp: 250°C)

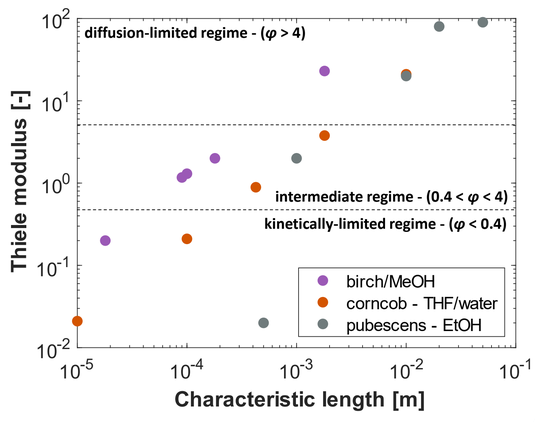
Grass (corncob) – THF/water system

- Size: 0.42mm – 0.18mm (Temp: 200°C)

Hardwood (*pubescens*) – ethanol system

- Size: 0.42mm – 0.18mm (Temp: 240°C)

- Kinetically-limited regimes assessed by the Thiele modulus.
- The characteristic length corresponds to the one of axially-oriented pores.
- Rate coefficients are estimated via regression of available experimental data.



Parameter estimation

- Values are statistically significant and in good agreement with reported data.
- Repolymerization reactions are important to fit the model against experimental data.

Rate coefficients and effective diffusivities

System	MW (Da)	Temperature (°C)	Parameter (bold: calculated through correlations) k_f (10^8)	k_r (10^3)	D_{eff} (10^{10})
birch – MeOH	1992	220	2.27 ± 0.10	0.37 ± 0.07	**4.79**
		230	2.71 ± 0.40	5 ± 4	**4.94**
		240	3.21 ± 0.51	4 ± 3	**5.08**
		250	5.06 ± 0.57	6 ± 3	**5.21**
corncob – THF/water	706	200	7 ± 3	44 ± 25	**6.25**
pubescens – ethanol	1532	240	4.16 ± 0.98	614 ± 163	**0.98**

References

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Acknowledgments

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Concluding remarks

- The reaction-diffusion model is versatile and can be applied to different solvolytic environments and different types of lignocellulosic biomass.
- Rate coefficients of repolymerization reactions have more uncertainty since the overall degree of delignification is primarily driven by solvolysis.
- Rate coefficients of repolymerization are important for determining kinetically-limited regimes.

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