

# Modeling biomass refining processes with classical chemical reaction engineering methods – challenges and opportunities

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## **Highlights**

- Chemical and physical inhomogeneity of biomass was considered with distributed variables
- Reaction-diffusion model for wood chips was developed to predict delignification and its variability
- Stochastic graphs were used to predict lignin macromolecule fragmentation kinetics

## **1. Introduction**

The transformation from a fossil to a renewable carbon-based society requires deep understanding of chemical conversion and fractionation processes for biomass. This requires a combination of two relatively well-established fields: classical pulp production on one hand, and classical chemical reaction engineering, with its basis in chemical kinetics and catalysis, diffusion theory, and multiphase flow dynamics on the other. There are still challenges originating mainly from the complex biomass structure with inherent variability in its chemical and physical nature. In classical pulping, not only tree species vary, but there are further micro- to nano-scale distributed properties, as well as strongly anisotropic behavior. These originate from the growth location, which part of the tree the chips originate, whether it is early- or latewood part of the tree and so on. To properly account for all these variabilities, classical chemical reaction engineering tools need to be combined with proper chemical and physical distribution models, augmented with stochastic models on a molecular level to consider the chemical heterogeneity of the lignin macromolecule.

## **2. Methods**

A reaction-diffusion model for wood chips in pulping conditions was developed<sup>1,2</sup>, including discretized spatial geometry of the chips as well as discretization of chemical composition distributions. Spatial discretization was done with a control volume approach and chemical distribution with quadrature method of moments. As delignification proceeds, the chemical distributions were followed as a function of time. Experimental work for individual fiber kappa numbers (degree of delignification), reported in the PhD thesis of Ming<sup>3</sup>, was used to validate the model.

In the second part of the work, detailed delignification chemistry was modeled by using stochastic graphs<sup>4</sup>. This approach allows to follow complex lignin macromolecule fragmentation and dissolution during delignification using classical chemical kinetics of individual chemical bonds.

## **3. Results and discussion**

First, “uniform pulping” conditions were modeled. This includes small chip sizes without diffusional limitations, as confirmed by the Weisz-Prater condition and simulations with spatially discretized chips. Only earlywood part of the wood was used in the experiments. There was still a distribution of kappa numbers (degree of delignification), which required modeling of fiber scale lignin content distributions. The next step was to model real pulping conditions, including diffusional resistances in industrial size chips with chips from different parts of a tree. This additional variability required further consideration of the original lignin distribution. Examples of the predictions are shown in Figure 1.

In the second part of this work, stochastic graphs were used to model lignin fragmentation during pulping. Basic lignin monomers were used as the building blocks, and bonds between the monomers

were formed based on known typical lignin chemical structures. The formed lignin macromolecules were then decomposed based on known kinetics for most abundant  $\beta$ -O-4 bond. This enables following overall delignification fragmentation process. Delignification is known to slow down during pulping, as the most reactive structures are first decomposed with stable ones remaining. An illustration of a lignin fragment with monomer units is shown in Figure 2.

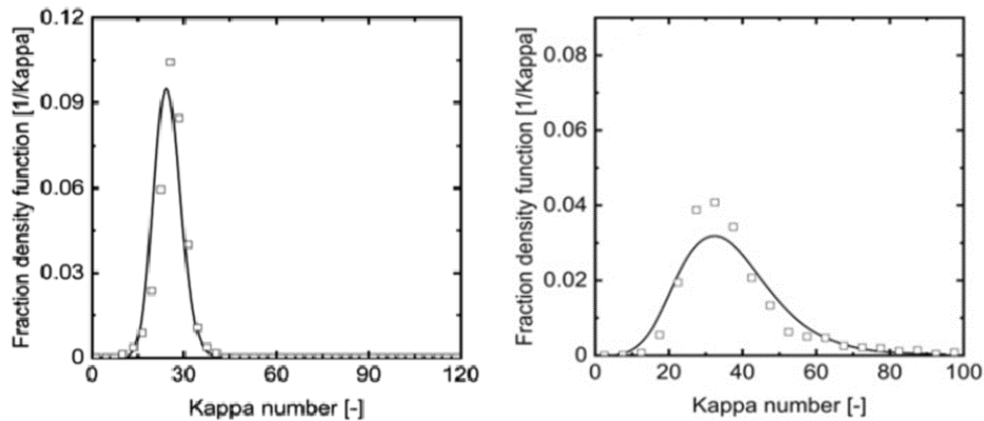


Figure 1. Model predictions for uniform pulping (left) and industrial conditions (right)<sup>1,2</sup>

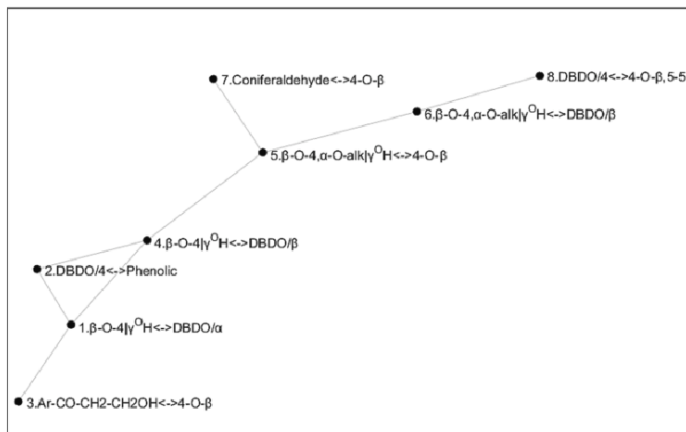


Figure 2. Graph representation of a lignin fragment with eight monomer units<sup>4</sup>

#### 4. Conclusions

Biomass refining processes could be modeled with classical chemical reaction engineering tools, but heterogeneous nature of the biomass needs to be carefully considered. The present work proposed two modeling approaches in different scales to allow detailed description of these processes. This enhances our understanding of the basic phenomena occurring in such complex reactive mixtures and allows to develop rigorous predictive models for future process development and design.

#### References

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#### Keywords

Biomass fractionation; distributed kinetics, reaction-diffusion model