

## Kinetic analysis of delignification of cedar wood during organosolv using 1-butanol

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### Highlights

- Distribution of lignin in cell wall showed peak-top located on center.
- The distributions were becoming sharper with reaction time.
- Unreacted-core model was applied for kinetic analysis for delignification.
- Diffusion in layer of product limiting model well expressed the result of delignification.

### 1. Introduction

Recently, lignocellulose biomass has attracted as new carbon resources. Separation of the biomass components, which are cellulose, hemicellulose, and lignin, is necessary for biorefinery, and some separation techniques have been developed for long years. Especially, organosolv method, in which a mixture of water and organic solvents is used for depolymerization of lignin and hemicellulose, has been focused on due to its potential for contribution to biorefinery. Generally, the reaction conditions of organosolv method are milder than those of other methods and this can suppress recombination of lignin fractions during delignification. This property of the method brings the possibility for effective use of lignin. Many researchers have investigated kinetics of delignification and pointed out the effect of mass transfer on the delignification rate [1]. However, no one have modeled the rate of delignification including effects of chemical reaction and mass transfer. In this study, we have tried to model kinetics of delignification on organosolv method using 1-butanol [2-3] by unreacted-core model [4], as shown in Figure 1. This model is used to express situations in which solid particles are being consumed by reactions, and the amount of the material being consumed is shrinking.

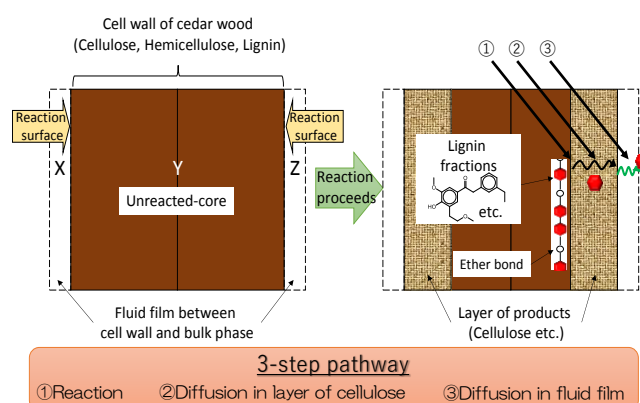


Figure 1. Unreacted-core model (Slab-type)

### 2. Methods

Delignification of cedar wood was carried out in a water/1-butanol mixture with/without silica-alumina catalyst using batch reactor at 473 K for 2-8 h. The molar ratio of water to 1-butanol was adjusted 1:4. After delignification, the products were filtered and divided into liquid and solid products. The solid products were dried, and then analyzed using elemental analyzer to measure carbon content. Chemical composition of cedar wood and the solid products were decided by NREL method [5]. Yields of the solid products and conversion of lignin ( $X_L$ ) were calculated on the basis of carbon. Moreover, lignin distribution of cell wall in cedar wood and the solid products were measured by raman spectroscopy [6]. Kinetics of delignification was studied using the following unreacted-core model equations: (a) Reaction on the surface of unreacted core and/or diffusion in fluid film limiting model;  $kt=X_L$ , (b) Diffusion in layer of the product

limiting model;  $kt=X_L^2$ , where  $k$  [ $h^{-1}$ ] is apparent rate constant,  $t$  [h] is reaction time, and  $X_L$  [C-mol%] is conversion of lignin.

### 3. Results and discussion

Figure 2 shows the distributions of lignin in cell wall of cedar wood and the solid products obtained from organosolv without catalyst. It indicated that delignification was proceeding with reaction time from outside to inside of cell wall. Moreover, it was confirmed that few amounts of cellulose were decomposed into the solvents during the delignification. Therefore, kinetics of the delignification was analyzed by unreacted-core model considering cell wall as unreacted-core and cellulose as layer of product. Figure 3 shows the plots of delignification rate by equation (a) and (b), respectively. This indicated that the results of (b) Diffusion in layer of product limiting model showed better linearity than (a) Reaction and/or Diffusion in fluid film limiting model when comparing each plot's  $R^2$  value. It means that the diffusion of the lignin fractions produced during the delignification is rate limiting step of the delignification on this organosolv.

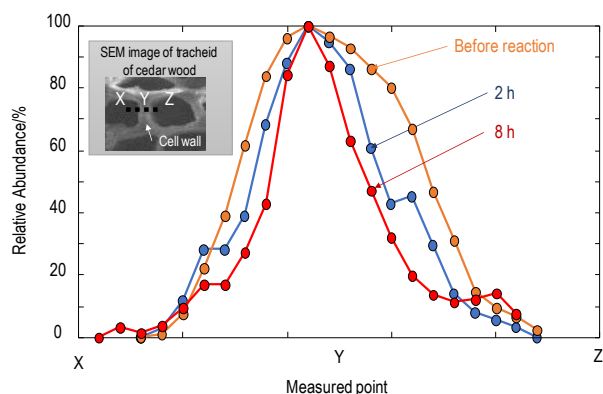


Figure 2. Distributions of lignin in cell wall before and after reaction

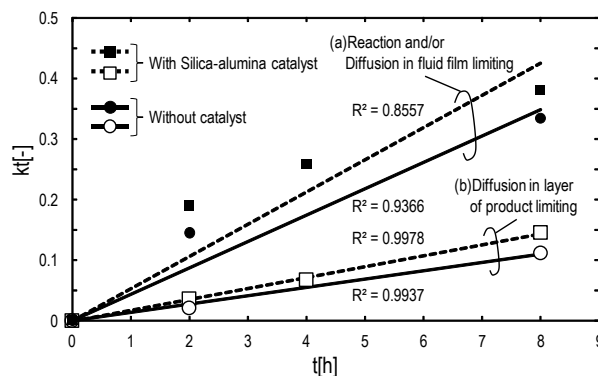


Figure 3. Plots of unreacted-core model

### 4. Conclusions

In this study, we applied unreacted-core model for analyzing kinetics of delignification on organosolv method using 1-butanol. As the result, it was supposed that rate limiting step of the delignification was diffusion of the lignin fractions in layer of product (cellulose).

### References

- [1] C. Mattsson, *et al.*, *Holzforchung*, 71 (2017) 545-553.
- [2] T. Yoshikawa, *et al.*, *Fuel Process. Technol.*, 108 (2013) 69-75.
- [3] T. Yoshikawa, *et al.*, *Appl. Catal. B-Environ.*, 146 (2013) 289-297.
- [4] H. Scott Fogler, *Elements of Chemical Reaction Engineering*, fourth ed., Pearson Education, London, 2005, pp. 792-800
- [5] Technical Report: Determination of Structural Carbohydrates and Lignin in Biomass. NREL/TP-510-42618; Natural Renewable Energy Laboratory: Golden, 2011; <http://www.nrel.gov/docs/gen/fy13/42618.pdf>
- [6] T. Kanbayashi, *et al.*, 69 (2015) 273-279

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### Keywords

“Lignocellulose biomass”, “Organosolv”, “Delignification”, “Unreacted-core model”