

Kinetic modeling study of lignocellulose fractionation using 4-phenolsulfonic acid ^{*}

Hyun-Kyu Choi^{*} Anqi Ji^{**} Mairui Zhang^{**} Juhyeon Kim^{*}
Joseph Sang-Il Kwon^{*} Chang Geun Yoo^{**}

^{*} *Artie McFerrin Department of Chemical Engineering, Texas A&M University, TX 77840 USA (e-mail: kwonx075@tamu.edu).*

^{**} *Department of Chemical Engineering, State University of New York College of Environmental Science and Forestry, NY 13210 USA (e-mail: cyoo05@esf.edu)*

Abstract: In this work, kinetic models are developed to interpret the fractionation dynamics under varying pretreatment conditions. Specifically, aspen wood chip samples were prepared with three different dimensions for pretreatment using 72% 4-phenolsulfonic acid in an isothermal reaction vial. Then, the solid recovery and residual lignin content in the wood chip were measured, which was then utilized to estimate the model parameters. The effects of biomass size and temperature on the solubilization and delignification kinetics are discussed and assessed for further utilization.

Keywords: fractionation; aspen wood; kinetic modeling; kinetics; parameter estimation; delignification

1. INTRODUCTION

With the global depletion of petroleum resources and emerging pollution, lignocellulosic biomass has been introduced as a promising resource for alternative fuels, chemicals, and materials because of its sustainability and renewability. Over the last several decades, biomass conversion technologies have been significantly improved; however, those biomass-derived products are still not cost-competitive compared to petroleum-derived products. The biorefinery concept has been proposed to maximize the utilization of biomass components by covering an extensive range of combined technologies for a wide range of value-added products like today's petrorefineries (Morais et al., 2015). This approach expands the use of biomass components from cellulose alone to entire biomass, including hemicellulose and lignin, to enhance the economic feasibility of biomass utilization.

Lignin is the largest non-carbohydrate component in the plant cell walls. It has been reported as a major recalcitrant factor in many biological conversion processes. It is shown in Yoo et al. (2020) that lignin interferes with the biological conversion of cellulose by limiting cellulose access as a physical barrier, non-productive binding to enzymes, and inhibiting microorganisms' activities. Therefore, it is necessary to remove or modify lignin prior to the biological conversion processes. In this regard, pretreatment is an essential step to reduce the recalcitrance factors. Various pretreatment methods using acid, alkaline, organic solvent and hot water have been investigated to increase the biomass conversion efficiency (He et al., 2020).

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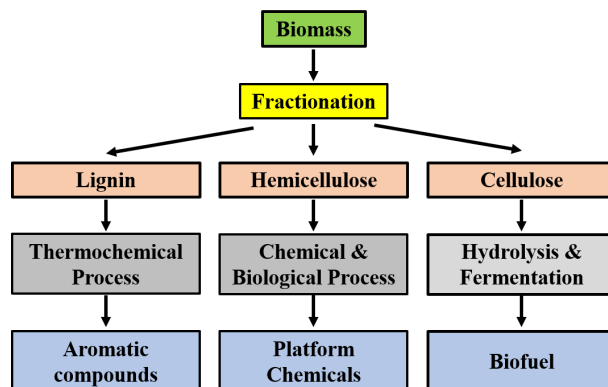


Fig. 1: A schematic illustration of fractionation process

However, harsh reaction conditions have caused the unwanted transformation of biomass components such as dehydration of the hydrolyzed sugars and condensation of lignin in many pretreatments. Recent pretreatment methods have been developed to maximize both carbohydrates (i.e., cellulose and hemicellulose) and lignin through effective fractionation (Fig. 1). These pretreatments achieved an effective delignification under relatively mild reaction conditions using organic co-solvent, ionic liquid, acid hydrotrope, and others (Meng et al., 2020). The dehydration of solubilized hemicellulose and condensation of lignin were significantly reduced, while a certain degree of lignin modification was unavoidable.

Motivated by the limitation, in our previous study, 4-phenolsulfonic acid (PSA) was considered for an effective fractionation of poplar wood chips. In this pretreatment, PSA not only performs as a catalyst but is also used as a solvent (Yoo et al., 2020). PSA has a unique perfor-

mance due to its amphiphilic structure composed of a hydrophobic benzene ring and a hydrophilic sulfonic acid together. It could cluster and aggregate with lignin in water due to this amphiphilic property. In addition, PSA could solubilize the lignin fragments by accumulating them via a hydrophobic effect. As a result, cellulose and lignin were effectively fractionated from poplar wood chips under mild temperature (50 – 80°C) and atmospheric pressure using PSA.

Even though the fractionation of lignocellulose has improved significantly by developing such novel agent for delignification, these technologies are still at the early stages of industrialization. While experimental approaches (e.g., development of solvent and catalyst) have been widely proposed, the applications of systematic modeling and optimization techniques have received relatively small spotlight due to the lack of understanding on the dynamic behavior of fractionation. Recently, kinetic modeling has become an important tool in the analysis of chemical reaction system by virtue of the advanced computation performance (e.g., collection and processing of large amount of elementary data and regression of the relationship between system variables). In this sense, when it comes to these biomass utilization, there have been several approaches to mathematically elaborate wood chip treatment processes with multiscale modeling strategies (Choi and Kwon, 2020b; Son et al., 2020). Motivated by the improvement, the kinetics of degradation of lignocellulose under varying dimension is studied in this work, through a series of laboratory experiments using PSA solvent and a kinetic modeling approach.

The article is organized as follows: we designed an experiment to investigate the dynamic behavior of pretreatment under PSA (i.e., solubilization and delignification). Then, kinetic models are developed to capture the effect of pretreatment conditions (e.g., biomass thickness and reactor temperature), followed by estimation of the model parameters by utilizing the experimental results. Lastly, the kinetic modeling results are discussed and the conclusion of the proposed work is provided.

2. MATERIALS AND METHODS

2.1 Materials

4-hydroxybenzenesulfonic acid (also known as 4-phenolsulfonic acid, PSA, 85 wt.%) is purchased from TCI AMERICA, and Aspen wood chips are supplied by SUNY ESF. The wood chips are air-dried and sliced into three different thicknesses (0.8, 3.0, and 5.0 mm). Specifically, the wood chips are Wiley-milled and screened using a 20-mesh sieve for 0.8 mm thickness samples, whereas wood chips with the thicknesses of 3 and 5 mm are manually trimmed with cutters. Prior to the experiment, the powder and chips are soaked in deionized water for 48 hours at room temperature. In this work, the moisture content of the soaked samples is measured.

2.2 PSA pretreatment of aspen wood chip

In the pretreatment experiment, 2.0 ± 0.3 g (dry weight) of water-soaked aspen samples are loaded to a 40 mL glass

reaction vial with a pressure-relief cap. Then, PSA (85 wt.%) is loaded into the reaction vial to make a 72 wt.% PSA solution with the water in the aspen sample. The reaction vial is placed in an oil bath at 70 – 90°C for 10 – 30 minutes. Upon the completion of the reaction, the softened aspen wood chips are manually disintegrated with glass stirring rods until jelly-like pulps are obtained. After skimming, the mixture is soaked in acetone for 20 minutes and filtrated. The solid residue is washed with acetone and water until the surface pH reaches 5. Both the solid residue and filtrate are collected and stored for further analysis. While treating the aspen samples with thickness of 0.8 mm, the mixture is directly soaked in acetone-water mixture (1:1, v/v) after pretreatment without manual disintegration.

2.3 Klason lignin analysis

Lignin content of biomass before and after pretreatment are measured according to NREL standard procedure (Sluiter et al., 2008). Specifically, untreated and pretreated wood chips are ground to 14 mesh prior to the analysis, and the size-reduced biomass is hydrolyzed by 72% sulfuric acid at 30°C for 1 hour and then diluted to 4% sulfuric acid by adding deionized water. The biomass and hydrolysate in 4% sulfuric acid are autoclaved at 121°C for 1 hour. After the two-stage hydrolysis, insoluble samples are filtered, washed by deionized water and oven-dried to quantify the acid-insoluble residue. After measuring the dry weight of acid-soluble residue, the samples are placed in the muffle furnace at 575°C for 24 hours. Lastly, the Klason lignin content are obtained by measuring deashed acid-soluble residues.

2.4 Model development

Since experiments are limited in analyzing the dynamic behavior of unmeasured conditions, in this work, kinetic models are developed by utilizing the experimental data, which is then employed to predict and further investigate the pretreatment dynamics. Specifically, the two kinetic models are capable of predicting the solid recovery and lignin content in pretreated biomass; the structure of models are adopted from references and the parameters of the models are estimated based on the experimental measurement.

Solid recovery During the fractionation process, cellulose is liberated while degrading and solubilizing solid components including lignin, hemicellulose and extractives (He et al., 2020). To evaluate the efficiency of the process, the weight loss of the solid phase is commonly measured; the amount of the residual solid (i.e., solid recovery) is proportional to that of cellulose, which is the most important value of pretreatment. Since the solubilization dynamics is affected by the dimension of reactant (i.e., wood chip), a kinetic model is developed to predict the solid recovery after the fractionation under the varying thickness of wood chip. By following previously developed assumptions, a conventional differential equation for the acid solubilization is developed in this work as follows:

$$\frac{dS_{re}}{dt} = -k_s(S_{re} - S_{re}^{\infty})^{\alpha} \quad (1)$$

where S_{re} is the solid recovery (%), k_s is the rate constant of the solubilization reaction, S_{re}^∞ is the unreactive fraction of the wood chip, and α is the reaction order.

While pretreating biomass, cellulose is relatively stable and resistant to acidic attack, leaving unreactive components when treated under a mild condition (Hendriks and Zeeman, 2009). The stable structure of cellulose is known to be responsible for the phenomenon under the given operating range, which has been captured by introducing an unreacting solid component in several kinetic models for delignification (Choi and Kwon, 2019a,b, 2020a). Similarly, the unreactive fraction term (S_{re}^∞) is included in the solubilization model of the proposed work to accurately capture the dynamic behavior.

Lignin content In conventional pulping processes (i.e., delignification), lignin has been considered as a low value by-product. However, recently, it has been suggested that lignin can be a valuable source of chemicals if it would be broken into smaller molecular units while preserving its stability. In other words, simultaneously removing the lignin from biomass and protecting the C-O bond of dissolved lignin is very important in lignocellulose fractionation process. In this work, PSA is applied for the pretreatment which is effective for this objective; PSA effectively dissolves the lignin fragments and secures the structure using its amphiphilic property. To evaluate the extent of delignification, an ordinary differential equation is employed to capture the delignification dynamics under PSA as follows:

$$\frac{dL}{dt} = -k_1L + k_2L_s \quad (2)$$

where L is the lignin content in biomass, L_s is the dissolved lignin content, k_1 and k_2 are the rate constants of delignification and condensation reaction, respectively. It is important to note that acid delignification is generally considered as an reversible first-order reaction (Dapí et al., 2002); experiments of delignification by acidic solvents at atmospheric pressure showed the condensation (i.e., reprecipitation) of lignin which is unfavorable for lignocellulose fractionation. The model parameters in (1) and (2) are estimated based on the experimental measurements, which are then utilized to analyze the underlying dynamics of pretreatment.

3. RESULTS AND DISCUSSION

3.1 Acid solubilization

In this work, PSA pretreatments are conducted with the three different thicknesses of aspen wood chips (i.e., 0.8, 3.0, and 5.0 mm) under the three different temperatures (i.e., 70, 80 and 90°C). During the pretreatment, PSA reacts with the biomass components and selectively dissolves hemicellulose and lignin, as discussed in our previous study (He et al., 2020). Table 1 presents the solid recovery after PSA pretreatment. By utilizing the measurements in Table 1, the parameters of (1) are estimated (i.e., rate constants and orders). Please note that while pretreating the 5 mm thickness wood chips, PSA did not show a significant biomass decomposition at 70°C for 10 – 30 minutes and 80°C for 10 minutes, resulting in the solid recovery of over 90%. Therefore, these conditions are not further studied in this work.

Table 1: Solid recovery after PSA pretreatment

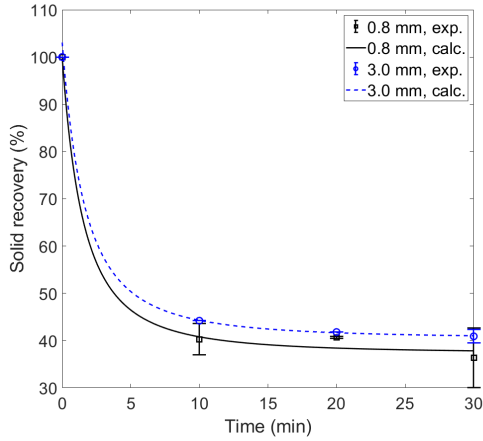
Thickness (mm)	Temperature (°C)	Time (min)	Solid recovery (%)
0.8	70	10	40.3 ± 3.3
		20	40.7 ± 0.2
		30	36.4 ± 6.3
	80	10	44.4 ± 3.6
		20	40.3 ± 2.5
		30	41.3 ± 0.3
	90	10	41.0 ± 2.7
		20	39.5 ± 0.2
		30	39.0 ± 0.3
3.0	70	10	44.2
		20	41.8
		30	40.9 ± 1.4
	80	10	43.6
		20	41.0 ± 1.0
		30	43.4
	90	10	43.6
		20	41.4
		30	39.3
5.0	70	10	NEGL
		20	NEGL
		30	NEGL
	80	10	NEGL
		20	55.2 ± 4.9
		30	53.2 ± 3.2
	90	10	NEGL
		20	56.5 ± 3.0
		30	54.6 ± 0.2

It is observed that the solid recovery under the identical temperature and time increases as the thickness of biomass increases (Fig. 2). In particular, the aspen wood of 5 mm thickness showed relatively higher solid recovery (Figs. 2b and 2c) and higher reaction order (Table 2) compared to those of 0.8 and 3 mm thicknesses. The two following factors are expected to be responsible for the observation. First, owing to the high thickness, PSA is not able to properly penetrate the biomass (i.e., aspen wood chip), thereby leaving the core of wood chip intact. Second, thick wood chips have longer pores that dissolved molecules have to diffuse, compared to thin wood chips. Accordingly, the dissolved bulky molecules in thick wood chips are more likely to be trapped in the cell matrix; pore size is known to significantly affect the lignin dissolution kinetics (Zhang et al., 2020). Moreover, the dissolved molecules are likely to adsorb onto the surface of cellulose-rich residue.

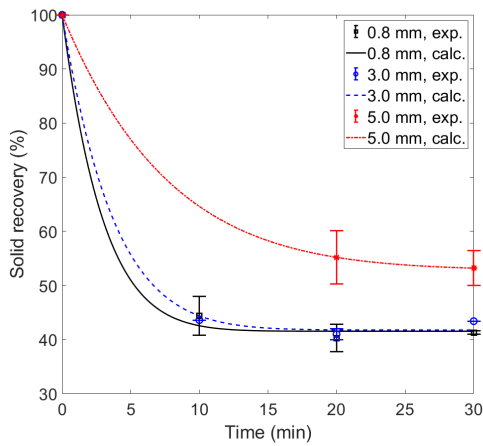
This interpretation is also supported by the estimated reaction rates in Fig. 3 and unreactive fraction of biomass in Fig. 4; small wood chips have relatively high reaction rates and small unreactive fractions. In addition, even though the unreactive fraction decreases along the diminishing thickness of biomass under the given condition,

Table 2: Solubilization reaction order

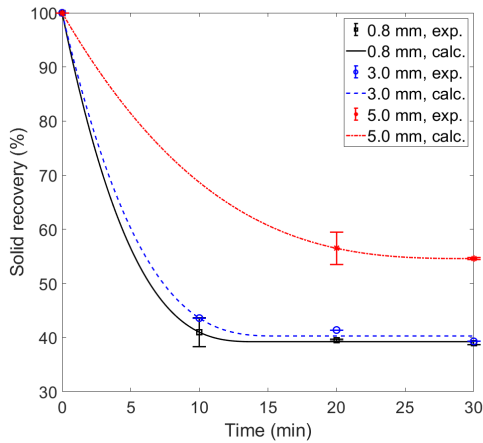
Thickness	0.8 mm	3.0 mm	5.0 mm
α	1.46	0.90	0.63



(a) Temperature = 70°C



(b) Temperature = 80°C



(c) Temperature = 90°C

Fig. 2: Experimental and predicted solid recovery under varying temperatures.

the unreactive fraction is expected to converge to a certain value even when the thickness is less than 0.8 mm. Since the high rigidity of cellulose-rich solids makes the cellulose stable under the given acidic condition, some portion of biomass remain unreacted regardless of reaction time; however, cellulose can be hydrolyzed to sugars under severe temperatures and high acidic conditions.

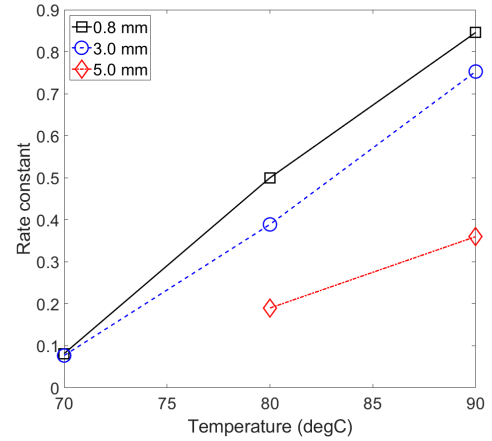


Fig. 3: Acid solubilization reaction constants under varying temperature and biomass size

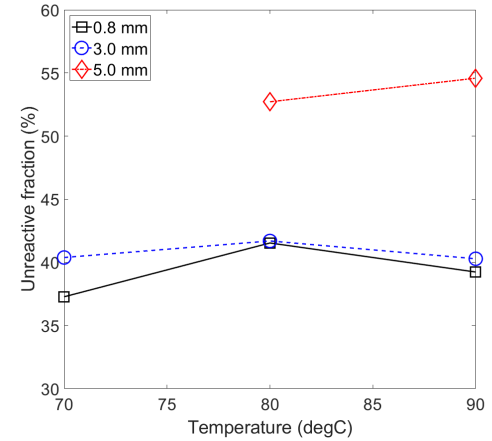


Fig. 4: Unreactive fraction of lignocellulose under varying temperature and biomass size

3.2 Delignification

In this work, the delignification kinetics of PSA pretreatment is studied by measuring Klason lignin content. Similar to the acid solubilization, the Klason lignin contents of the three different thicknesses of aspen wood chips (i.e., 0.8, 3.0, and 5.0 mm) under the three different temperatures (i.e., 70, 80 and 90°C) are measured for the analysis. The lignin content of untreated biomass is 19.6% and decreases during the PSA pretreatment as a result of delignification (Table 3). The parameters in (2) (i.e., delignification and condensation rate constants) are estimated based on the measurements, which are then embedded in the model to predict the trajectories of lignin contents. The profiles of predicted and measured Klason lignin content under the three different temperatures are demonstrated in Fig. 5, and the estimated model parameters are shown in Fig. 6.

Under the given operating condition, the pretreatment temperature plays an important role in determining the kinetics of delignification. At high temperatures, the Klason lignin rapidly reaches the equilibrium state where the delignification and condensation rates are equal. For example, the Klason lignin content of 0.8 mm thickness

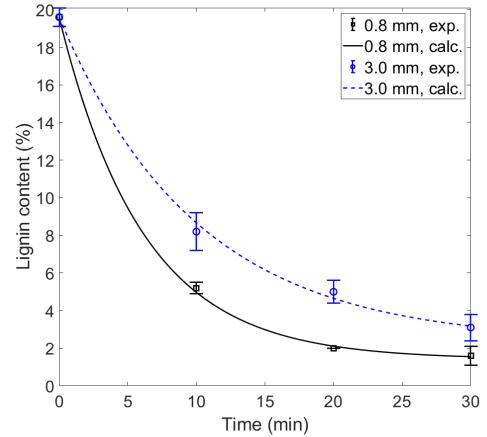
Table 3: Klason lignin content in wood chips after PSA pretreatment

Thickness (mm)	Temperature (°C)	Time (min)	Lignin content (%)
Untreated	-	-	19.6 ± 0.5
0.8	70	10	5.2 ± 0.3
		20	2.0
		30	1.6 ± 0.5
	80	10	2.4
		20	1.6
		30	2.1
	90	10	1.8
		20	1.8
		30	2.2
3.0	70	10	8.2 ± 1.0
		20	5.0 ± 0.6
		30	3.1 ± 0.7
	80	10	7.3 ± 0.7
		20	4.6 ± 0.3
		30	3.9
	90	10	4.9 ± 0.6
		20	2.2 ± 0.2
		30	1.5 ± 0.1
5.0	70	10	N/A
		20	N/A
		30	N/A
	80	10	N/A
		20	7.4
		30	5.9 ± 0.6
	90	10	N/A
		20	7.5 ± 0.1
		30	8.1 ± 0.3

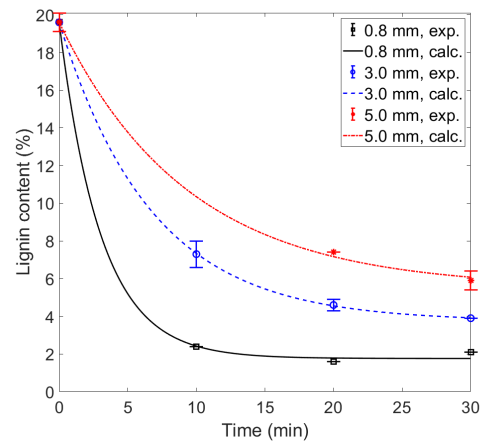
biomass no longer changes after 10 minutes at 90°C (Fig. 5c), whereas that in 70°C continuously decreases until 30 minutes of pretreatment (Fig. 5a). The rising lines in Fig. 6a clearly demonstrate the temperature dependence of delignification kinetics.

In addition, the delignification reaction is also dependent on the thickness of biomass; small thickness facilitates the removal of lignin during the PSA pretreatment (Fig. 5). Specifically, more than 70% of lignin in 0.8 mm thickness biomass is removed within 10 minutes for all the three temperatures and relatively small amount of lignin is removed during the rest of pretreatment period (black lines in Fig. 5). Similarly, in this experiment, the Klason lignin content increases as the biomass thickness grows at identical pretreatment times. It is because higher thickness wood chips have a smaller surface area which limits the mass transfer of PSA to the wood chips during the pretreatment. The higher delignification rates of the thinner biomass in Fig. 6a also support the interpretation; the reaction rates of 0.8 mm thickness is greater than those of 3.0 and 5.0 mm at the three temperatures.

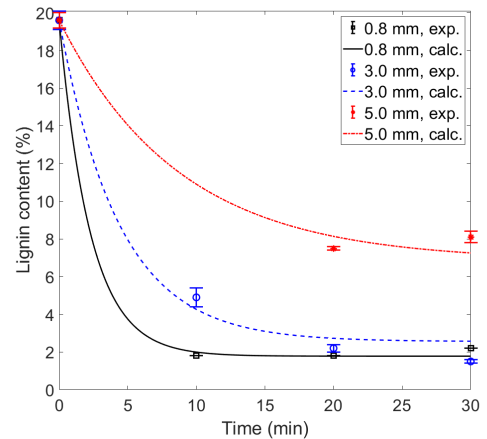
On the other hand, the condensation reaction shows a less significant correlation between the thickness of biomass. The three different colored lines in Fig. 6b are moderately overlapping with each other, implying the weak impact of the biomass thickness on the condensation kinetics. This observation might be attributed to the following interpretation.



(a) Temperature = 70°C



(b) Temperature = 80°C

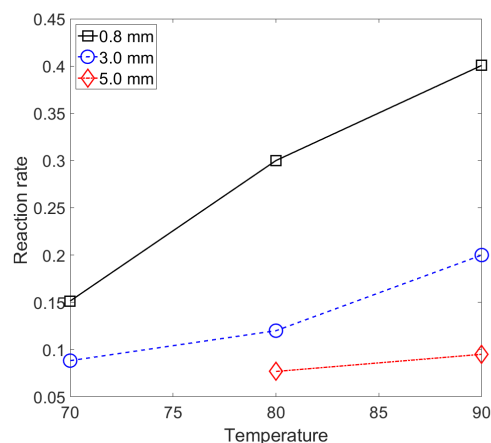


(c) Temperature = 90°C

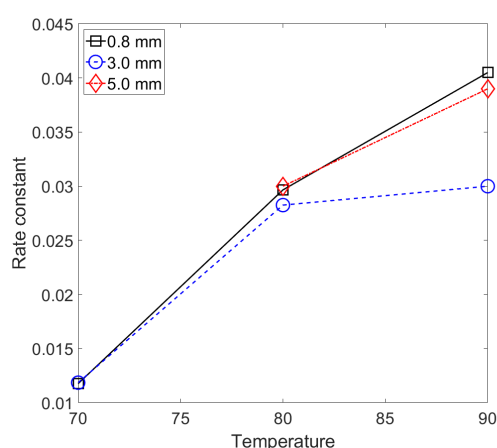
Fig. 5: Experimental and predicted residual lignin content under varying temperatures.

The condensation of lignin is mainly caused by the amount of repolymerized lignin (Shuai and Saha, 2017) and pseudo lignin, which is formed from the hydrolyzed and dehydrated carbohydrates under acidic conditions (Shinde et al., 2018). The pretreatment temperature is one of the major parameters to govern the condensation rate. In this study, the lignin condensation is possible regardless of thickness as most of hemicellulose and lignin are dissolved

REFERENCES



(a) Delignification reaction constants



(b) Lignin condensation reaction constants

Fig. 6: Reaction kinetics of lignin under varying temperature and biomass size

within 10 minutes of the PSA pretreatment, and the increase in Klason lignin content is observed at the latter half of the PSA pretreatment in some cases (e.g., 0.8 mm at 80°C and 5.0 mm at 90°C).

4. CONCLUSION

In this work, the fractionation dynamics was quantitatively examined by integrating the designed PSA pretreatment experiment and developed kinetic models. Specifically, first, aspen wood chips were prepared in three different thicknesses and pretreated in PSA at three different temperatures, followed by measuring the solid recovery and Klason lignin content of biomass. Then, the parameters of the two kinetic equations which are describing the dynamic behaviors of solubilization and delignification, respectively, are estimated based on the experimental data and employed to interpret the effect of biomass thickness on the dynamics. The temperature and size dependence of PSA pretreatment is analyzed in this work, which would be further utilized to optimize the fractionation process by applying the proposed approach to other solvents and biomass types.

- Choi, H. and Kwon, J.S. (2019a). Modeling and control of cell wall thickness in batch delignification. *Computers & Chemical Engineering*, 128, 512–523.
- Choi, H. and Kwon, J.S. (2019b). Multiscale modeling and control of Kappa number and porosity in a batch pulp digester. *AIChE Journal*, 65(6), e16589.
- Choi, H. and Kwon, J.S. (2020a). Multiscale modeling and multiobjective control of wood fiber morphology in batch pulp digester. *AIChE Journal*, 66, e16972.
- Choi, H.K. and Kwon, J.S.I. (2020b). Multiscale modeling and predictive control of cellulose accessibility in alkaline pretreatment for enhanced glucose yield. *Fuel*, 280, 118546.
- Dapí, S., Santos, V., and Parajó, J.C. (2002). Study of formic acid as an agent for biomass fractionation. *Biomass and Bioenergy*, 22(3), 213–221.
- He, D., Wang, Y., Yoo, C.G., Chen, Q., and Yang, Q. (2020). The fractionation of woody biomass under mild conditions using bifunctional phenol-4-sulfonic acid as a catalyst and lignin solvent. *Green Chemistry*, 22(16), 5414–5422.
- Hendriks, A.T.W.M. and Zeeman, G. (2009). Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology*, 100, 10–18.
- Meng, X., Bhagia, S., Wang, Y., Zhou, Y., Pu, Y., Dunlap, J.R., Shuai, L., Ragauskas, A.J., and Yoo, C.G. (2020). Effects of the advanced organosolv pretreatment strategies on structural properties of woody biomass. *Industrial Crops and Products*, 164, 112144.
- Morais, A.R., da Costa Lopes, A.M., and Bogel-Lukasik, R. (2015). Carbon dioxide in biomass processing: contributions to the green biorefinery concept. *Chemical reviews*, 115(1), 3–27.
- Shinde, S.D., Meng, X., Kumar, R., and Ragauskas, A.J. (2018). Recent advances in understanding the pseudo-lignin formation in a lignocellulosic biorefinery. *Green Chemistry*, 20(10), 2192–2205.
- Shuai, L. and Saha, B. (2017). Towards high-yield lignin monomer production. *Green Chemistry*, 19(16), 3752–3758.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). Determination of structural carbohydrates and lignin in biomass. *Laboratory analytical procedure*, 1617(1), 1–16.
- Son, S.H., Choi, H.K., and Kwon, J.S.I. (2020). Multiscale modeling and control of pulp digester under fiber-to-fiber heterogeneity. *Computers Chemical Engineering*, 143, 107117.
- Yoo, C.G., Meng, X., Pu, Y., and Ragauskas, A.J. (2020). The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review. *Bioresource technology*, 301, 122784.
- Zhang, J., Chen, H., Ma, Z., Li, H., Dong, Y., Yang, H., Yang, L., Bai, L., Wei, D., and Wang, W. (2020). A lignin dissolution-precipitation strategy for porous biomass carbon materials derived from cherry stones with excellent capacitance. *Journal of Alloys and Compounds*, 832, 155029.