



# Kinetic modeling of sugar hydrolysis and degradation in SPORL Pretreatment

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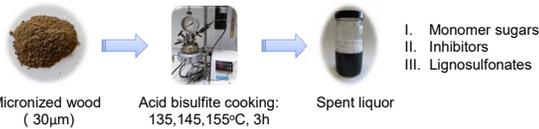
## Introduction

The inherent chemical recalcitrance of biomass promoted the development of pretreatment process. Especially, softwood has high lignin content and traditional methods such as dilute acid didn't perform as good as on grass biomass. Therefore, sulfite cooking have been introduced as pretreatment method for softwood materials. There are many types of cooking methods, such as alkaline sulfite, acid sulfite and neutral sulfite. Acid sulfite cooking was widely used in pretreatment process due to its high percentage hydrolysis of hemicellulose and partial lignin removal. Sugars go through several types reactions during sulfite cooking process. Polysaccharides can be hydrolyzed into monomer sugar and monomer sugar can be further degraded into inhibitors. In order to achieving high sugar recovery and decreasing hazardous environment caused by inhibitors, understanding yield curve of monomer sugar and inhibitors will be significantly important.

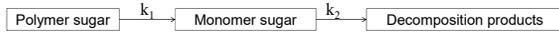
## Objective

The objective of this present study is to investigate the kinetics of polymer sugar hydrolysis and monomer sugar decomposition process and investigate the inhibitors formation during pretreatment process. Also, lignosulfonates yield in spent liquor was investigated along with treatment time to characterize lignin removal during pretreatment process.

## Material & Method



In order to characterize multiple products kinetics in bisulfite cooking process, Seaman model and Arrhenius equation were employed to calculate the reaction rate constants.



• Seaman Model

• Arrhenius Equation

$$M = \left[ \frac{k_1 P_0}{k_2 - k_1} \right] (e^{-k_1 t} - e^{-k_2 t})$$

$$k_i = k_{i0} e^{-\frac{E_a}{RT}}$$

Where:

M: sugar concentration, g/L

Po: Initial sugar concentration, g/L

k<sub>1</sub>: rate constant, min<sup>-1</sup>

k<sub>2</sub>: rate constant, min<sup>-1</sup>

t: time, min

Where:

k<sub>i</sub>: Kinetic coefficient (i = 1 or 2), min<sup>-1</sup>

k<sub>i0</sub>: Pre-exponential factor (i = 1 or 2), min<sup>-1</sup>

E<sub>a</sub>: Activation Energy, kJ mol<sup>-1</sup>

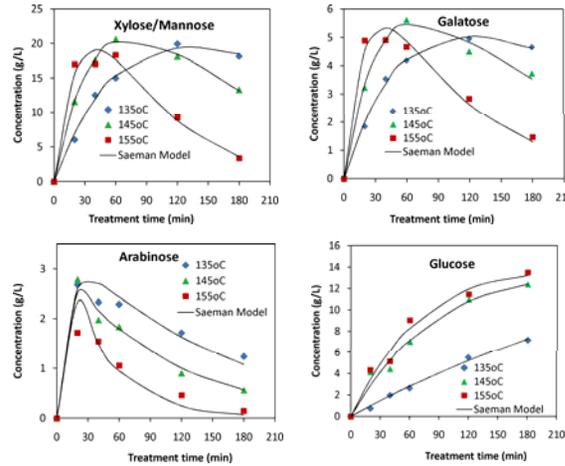
R: Gas Constant, 8.314 J mol<sup>-1</sup>K<sup>-1</sup>

T: Temperature, K

Table 1 Experimental design

Temperature (°C)	Cooking time (min)				
	20	40	60	120	180
135	1. Sugars, LS, HMF & furfural by analysis of spent liquor;				
145	2. Solid recovery, residual lignin & thermal analysis of treated solids;				
155	3. Enzymatic digestibility of treated solids;				

## Sugar concentrations in the pretreated liquors with the progress of pretreating time



- Obtain k<sub>1</sub> and k<sub>2</sub> with above data through Saeman model fitting for monomer sugars.
- Glucose didn't have a complete hydrolysis and degradation curve during 3 hours cooking.

## Activation energy and pre-exponential factors

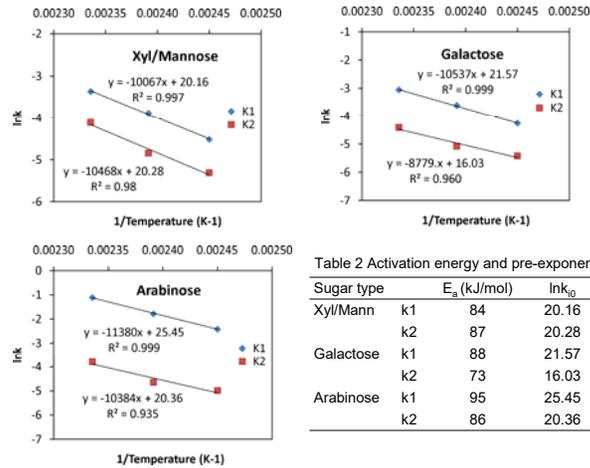
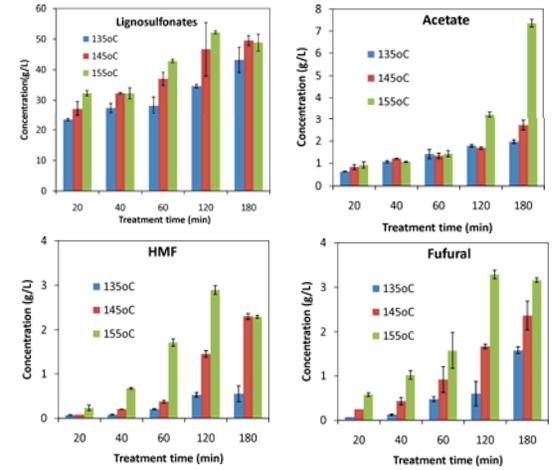


Table 2 Activation energy and pre-exponential factor

Sugar type		E <sub>a</sub> (kJ/mol)	lnk <sub>0</sub>	R <sup>2</sup>
Xyl/Mann	k1	84	20.16	0.998
	k2	87	20.28	0.978
Galactose	k1	88	21.57	0.999
	k2	73	16.03	0.960
Arabinose	k1	95	25.45	0.999
	k2	86	20.36	0.935

## Lignosulfonates and sugar degradation products



- Inhibitor formation increased along with treatment temperature and time. HMF concentration decreased at 3h treatment compared to 2h.
- Lignosulfonates concentration increased along with treatment time and temperature. However, no significant difference between 145 and 155°C at 3h treatment.

## Conclusions

- The rates of polymer sugar hydrolyzed to monomer reactions have a following order: Xylan/Mannan > Galactan > Arabinan
- The rate of degradation reaction have a following order: Galactan > Arabinan > Xylan/Mannan
- High temperature increased degradation rate of monomer sugar.
- Xylose/mannose yield in spent liquor reached maximum at 145°C and 1h treatment.
- Maximum total sugar recovery ( including sugar from spent liquor and enzymatic hydrolysis) can be achieved at 145°C and 2h, and this temperature was also preferred in Gao and Zhu's studies.
- Inhibitor formation increased along with treatment temperature and time.

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