



# A novel kinetic model for polysaccharide dissolution during atmospheric acetic acid pretreatment of sugarcane bagasse



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## HIGHLIGHTS

- A novel kinetic model for polysaccharide dissolution during acetic acid pretreatment.
- “Potential dissolution degree” was introduced based on cell wall structure.
- The presence of acetic acid accelerate polysaccharide dissolution.
- Acetylation of cellulose and xylose was observed.

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## ABSTRACT

Acetic acid (AcH) pretreatment of sugarcane bagasse with the catalysis of sulfuric acid (SA) could greatly enhance the enzymatic digestibility of cellulose. However, polysaccharide dissolution happened inevitably during the pretreatment. It was found that the simplest model, which assumes that the total polysaccharides were reactive to be dissolved, could not well describe the kinetic behavior of polysaccharide dissolution. A novel pseudo-homogenous kinetic model was thus developed by introducing a parameter termed as “potential dissolution degree” ( $\delta_d$ ) based on the multilayered structure of cell wall. It was found that solid xylan and glucan dissolutions were a first-order reaction with respect to the dissolvable fraction. Due to the delignification action of AcH, polysaccharide dissolutions were enhanced in AcH media compared with those in aqueous system. Acetylations of cellulose and sugars were also observed, and AcH concentration showed a significant influence on the degree of acetylation.

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## 1. Introduction

Production of fuel ethanol from lignocellulosic biomass has been considered as a promising direction for a sustainable production of liquid biofuels. However, the conversion processes are far more complex and sophisticated because of the recalcitrant nature of lignocelluloses, and breaking the recalcitrant structure and releasing sugars are considered as one of the major barriers to the commercialization of cellulosic ethanol (Huang et al., 2011). Therefore, pretreatment is a prerequisite step to obtain a good enzymatic digestibility of cellulose. Various pretreatment techniques have been developed during last decades as reviewed by a number of papers (Sun and Cheng, 2002; Mosier et al., 2005; Yang and Wyman, 2008; Hendriks and Zeeman, 2009; Kumar et al., 2009; Zhu et al., 2010; Zhao et al., 2012a). Among these techniques, the organosolv process, which refers to pretreatment of the biomass with various organic solvents or their aqueous solutions, has been considered as a “fractionating” process to increase cellulose digestibility and

obtain multiple products (Zhao et al., 2009). Organic acids, particularly formic acid and acetic acid have been used for pulping of lignocellulosic biomass, because that these acids have a strong solubility for lignin (Muurinen, 2000). Pretreatment of lignocellulosic biomass based on organic acid delignification has been found to greatly enhance the enzymatic digestibility of cellulose (Zhao and Liu, 2011; 2012), and direct recycling of the organic acid spent liquor for delignification shows no significant decrease of pretreatment efficiency but greatly reduces the energy consumption for solvent recovery (Zhao and Liu, 2012). Another advantage associated with organic acid pretreatment is that hemicelluloses can be hydrolyzed into sugars which can be further converted to derivative chemicals such as furfural under the catalysis of the residual organic acid at a high temperature. Therefore, understanding the kinetic behaviors of polysaccharide dissolution during organic acid pretreatment is important, which can serve as a tool for further optimizing and controlling the process.

Some studies have reported the kinetics of polysaccharide hydrolysis during organosolv pulping or pretreatment of lignocellulosic biomass (Vázquez et al., 1995; Parajó et al., 1995a,b; Abad et al., 1997; Küçük and Demirbaş, 1999; Dapía et al., 2002; Sidiras

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## Nomenclature

AcH	acetic acid	$G_S$	dissolution ratio of solid glucan (cellulose)
$C_{SA}$	sulfuric acid concentration, mol/L	$k$	dissolution rate constant, $h^{-1}$
$C_{AcH}$	acetic acid concentration, wt% or mol/L	SA	sulfuric acid
$\delta_d$	potential dissolution degree	$T$	temperature, K
$E_a$	activation energy for polysaccharide dissolution, kJ/mol	$X_S$	dissolution ratio of solid xylan

and Sidirasa, 2004; Shatalov and Pereira, 2005; Villaverde et al., 2010). In these studies, the polysaccharide dissolution/hydrolysis was considered as a pseudo-homogeneous irreversible first-order reaction with respect to the residual polysaccharide content. Being similar to the kinetics of dilute acid hydrolysis of polysaccharide, the kinetics of polysaccharide hydrolysis during organosolv pretreatment are usually described by Saeman's model or two-fraction model (Zhao et al., 2012b). Saeman's model is the simplest one which assumes that polysaccharide dissolution is a process involving a direct hydrolysis of polysaccharide into monosaccharides (Saeman, 1945) (Scheme 1). However, many research works have proved that Saeman's model must be modified to more accurately describe the hydrolysis of lignocellulosic polysaccharide. One of the well-known modified models is the two-fraction model, which assumes that the cell wall polysaccharide consists of two fractions: fast (easy) and slow (difficult) hydrolyzing fractions (Scheme 2). These fractions shows different hydrolysis rates during pretreatment, and a parameter  $\alpha$ , defined as the mass ratio of easy-to-hydrolyze fraction to the total polysaccharide is introduced into the kinetic models. However, it was found that the easy-to-hydrolyze and difficult-to-hydrolyze fractions were defined for the convenience of rate constant calculations and have not been correlated to any physical or chemical characteristics of the raw material (Lavarack et al., 2002). Another problem associated with the current kinetic modeling of polysaccharide dissolution in organosolv pretreatment is that the relations between kinetic constants and reaction severities (temperature, catalyst and solvent concentrations) have not been established. Therefore, these models cannot be widely used to predict the degree of polysaccharide dissolution under different pretreatment conditions.

In a previous work, a novel pseudo-homogeneous kinetic model for acetic acid (AcH) delignification of sugarcane bagasse by introducing the parameter of "potential degree of delignification ( $d_D$ )" was proposed based on the multilayered structure of plant cell wall and the inhibitive effect of dissolved lignin on delignification rate (Zhao and Liu, 2013).  $d_D$  was a function of pretreatment temperature, catalyst ( $H_2SO_4$ ) and AcH concentrations. It was defined as the potential maximum degree of delignification at a certain reaction severity. The model-predicted data showed very good accordance with the experimental data. Therefore, in the present work, a similar model by introducing the parameter of "potential dissolution degree ( $\delta_D$ )" has been proposed to describe the kinetic behaviors of polysaccharide dissolution during AcH pretreatment of sugarcane bagasse. The effects of temperature,  $H_2SO_4$  and AcH concentrations on dissolution rates and degrees of xylan and glucan (the main polysaccharides of sugarcane bagasse) are further analyzed.

## 2. Methods

### 2.1. Raw materials

Sugarcane bagasse used in the experiments was obtained from Guangxi Zhuang Autonomous Region in South China. It was air-dried and screened. The part that could not pass through 20-mesh

sieve was collected for AcH pretreatment. The main components of the bagasse were determined to be 42.1% glucan, 23.5% xylan, 1.2% arabinose, 2.4% acetyl group, 24.7% klason lignin and 1.0% acid-soluble lignin. The standard compounds used for HPLC calibration, including glucose, xylose and arabinose, were purchased from Sigma–Aldrich (Shanghai agent).

### 2.2. Pretreatment process

The delignification process was carried out in a 1000 mL three-neck glass flask heated by electric jacket or water bath under atmospheric pressure with one of the neck connecting with a condenser. 30 g of screened bagasse was packed into the flask followed by addition of 300 mL 60–90 wt% AcH solution with 0.1–0.4 wt% sulfuric acid (SA, based on liquid). Electrical stirring with a Teflon paddle was used at 300 rpm for keeping the system as homogeneous as possible. After delignification the solid was recovered by suction filtration. The obtained solid was first washed with 300 mL 60–90 wt% AcH solution and then filtered under pressure to remove as much liquid as possible. The solid was then washed with water until neutrality and dried for further analysis.

### 2.3. Analytical methods

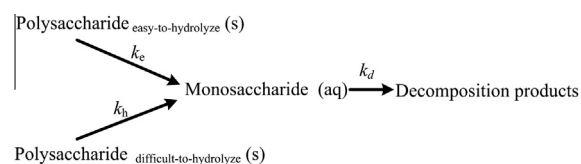
The main components of the bagasse and pretreated solid were determined according to NREL's Laboratory Analytical Procedure (Sluiter et al., 2008). The monosaccharides and AcH concentrations were determined by Shimadzu (Tokyo, Japan) HPLC (LC-10AT) system as described in the previous work (Zhao et al., 2012b). For determination of the monosaccharides in spent liquor, 50  $\mu$ L spent liquor was diluted with 950  $\mu$ L deionized water. The mixture was then centrifuged at 14,000 rpm to remove the precipitated lignin. The supernatant was then analyzed by HPLC after diluted by ten times. It should be noted that the monosaccharides, especially xylose, can be acetylated during pretreatment, which resulted in several new HPLC peaks. This phenomenon became more significant at a high AcH concentration.

### 2.4. Data processing

The kinetic constants were regressed according to the experimental data by nonlinear fitting with Matlab 6.5 software to



**Scheme 1.** The simplest model for polysaccharide hydrolysis (Saeman's model).



**Scheme 2.** The two-fraction model for cell wall polysaccharide hydrolysis.

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