



# Impact of cationic polyelectrolyte on the nanoshear hybrid alkaline pretreatment of corn stover: Morphology and saccharification study



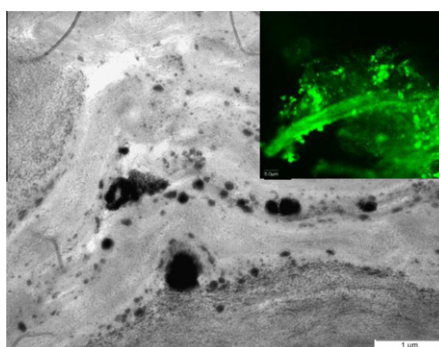
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## HIGHLIGHTS

- ▶ The addition of polyelectrolyte in the pretreatment greatly modified the lignin in the biomass.
- ▶ It further induced the morphological changes of cell wall layers.
- ▶ Both glucose and xylose yields were enhanced in the enzymatic hydrolysis.
- ▶ Lignin migrated, redistributed, and formed globular complex.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Cationic polyelectrolyte was first used as the additive in the nanoshear hybrid alkaline pretreatment of corn stover. The novel nanoshear hybrid pretreatment process was recently developed at MSU. The chemical compositions and morphologies were investigated by SEM, TEM, confocal CLSM, and XPS to elucidate the degradation mechanism of cellular structures. At room temperature and fast processing conditions (~2 min), lignin was found to redistribute on the inner and outer surfaces of the cell wall as lignin aggregate droplets instead of being extracted. Free microfibrils in the residues were also observed. The yields of enzymatic hydrolysis were enhanced for the pretreated corn stover with the aid of polyelectrolyte as an additive. We speculate that lignin was effectively modified which opened up the cell wall structure during the short pretreatment process and prevented non-productive binding of enzymes in the enzyme hydrolysis reaction.

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## 1. Introduction

The need for alternative renewable fuel is urgent because of the increasing energy supply concerns and the problem of CO<sub>2</sub> emissions. The production of ethanol as biofuel from lignocellulosic biomass is one of the most feasible options in terms of production scale and market value (Duff and Murray, 1996). Enzymatic hydrolysis is considered the most promising and also extensively studied technology in bioenergy processes, because of its mild and specific

characteristics. However, currently a rapid and effective conversion of lignocellulosic materials to fermentable sugars by enzymatic hydrolysis is still hard to obtain (Wyman, 2007). Additionally lignocellulosic biomass is inherently recalcitrant to enzymes due to its complex and robust cell wall structure. Therefore, the pretreatment process needs to be performed to fractionate lignocellulosic components into a digestible form and also to integrate the production of high-value added co-products into the bio-refinable fuel and power output (Mosier et al., 2005; Xu et al., 2012). Since the pretreatment and the enzymatic hydrolysis are key processes for successful production of cellulosic ethanol, major concern is put on the large consumption of enzymes and costly pretreatment needed to maximize ethanol yields.

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Pretreatments such as biological, chemical, physical, and thermal processes aim to disrupt the naturally resistant shield of lignin and to increase the accessibility of enzymes to cellulose and hemicellulose (Li et al., 2012; Mosier et al., 2005). One of the promising approaches is the utilization of chemical additives, such as inorganic salts and surfactants, to improve the efficiency of enzymatic hydrolysis (Kumar and Wyman, 2009b). For example, surfactants, especially non-ionic surfactants, have been applied after the biomass pretreatments to enhance the cellulose hydrolysis as well as to decrease the enzyme loading (Kim et al., 2007). The positive effects of the addition of surfactants have been proposed to increase the availability of enzymatic reaction sites, to reduce the enzyme denaturation, and to remove the recalcitrant lignin, etc., (Eriksson et al., 2002). Attempts have also been made by investigating the effect of surfactants on the pretreatment process which showed the prevention of unproductive bindings of enzymes to lignin and thus increased enzymatic hydrolysis yields (Qing et al., 2010).

Several studies have reported the utilization of inorganic salts in the biomass pretreatments as it successfully accelerates the degradation of cellulose and hemicellulose and improves the sugar yields (Liu et al., 2009; Monavari et al., 2011). Liu et al. have applied various inorganic salts on the pretreatment of corn stover without the addition of other chemicals (Liu et al., 2009). They found that the amount of hemicellulose removal from the solid part to the liquor was greatly increased when corn stover was treated with ferric chloride ( $\text{FeCl}_3$ ). Most of the monomeric and oligomeric sugars in the liquor could be recovered. The pretreated corn stover turned out to be softer and more digestible.

Cationic polyelectrolytes as good strength additives and retention agents have attracted a considerable interest in the paper industry (Burke et al., 2011; Li and Pelton, 1992). The cationic polyelectrolytes have good adsorption properties onto cellulosic fibers contributed by electrostatic interactions (Wagberg, 2000). Mora et al. proposed a patching mechanism for the enhancement of cellulase hydrolysis rate in the presence of cationic polyacrylamide (c-PAM), where c-PAM inhibited the charge repulsion and increased the binding between fibers and enzymes (Reye et al., 2011). The use of cationic polyelectrolytes in the kraft pulping process as flocculation agents was based on the study of interactions between these polymers and lignin under various solution conditions (Burke et al., 2011). Li and Pelton have shown the successful removal of kraft lignins with polyamines or poly(diallyldimethylammonium chloride) (PDAC) at high pH where carboxyl groups in the lignin chains were dissociated and formed the macroscopic complexes with PDAC (Li and Pelton, 1992). They used the polycations to precipitate the lignin out from the kraft lignin solution. They claimed in the paper that the complexes are lignin/polycation complex formed by electrostatic attraction of oppositely charged macromolecules. Recent studies in terms of the saccharification rate and pulp washing are advancing their potential as efficient additives for lignocellulosic ethanol production (Mora et al., 2011; Reye et al., 2011). However, as far as we know, there is no study applying polyelectrolytes as additives for biomass pretreatment to date. The pretreatment processes usually take from hours to days long, still requiring the improvement to achieve high effectiveness and efficiency for pretreatment itself and subsequent operations. In addition, little investigations on morphological changes of treated fibers or biomass have been carried out regarding to the addition of polyelectrolytes.

In this regard, the main purpose of this study is to evaluate the effectiveness of cationic polyelectrolytes on the pretreatment process with alkali in the nanoshear hybrid pretreatment process which was recently developed by our group (Lee et al., 2012; Wang et al., 2013). The novel pretreatment based on our high shear flow nanomixing reactor has been reported to greatly fractionate ligno-

cellulosic components from cell wall matrix. PDAC was selected as a strong, positively charged polyelectrolyte, which has been commonly used to modify the cellulose surface and stabilize the lignin. The investigation of biomass changes in composition and structure was studied and the effect on enzymatic conversion efficiency was also reported.

## 2. Methods

### 2.1. Materials

The premilled Michigan grown corn stover (CS) samples (1–2 mm) were obtained from Metna Corporation (Lansing, MI). The enzyme Accellerase 1000 was a complex of exoglucanase, endoglucanase, hemicellulase and beta-glucosidase (Danisco US Inc., Genencor Division, Rochester, NY) with enzyme activity of 46.92 FPU/mL determined by Purdue University. Sodium citrate (Dihydrate, Granular) and citric acid (Monohydrate, Granular) were purchased from J.T. BAKER and used as received. Sodium hydroxide was purchased from Spectrum Chemical MFG. Corp and used as received. Cationic polyelectrolyte, poly(dimethyldiallylammonium chloride) (PDAC), (Mw 100,000–200,000), was purchased from Aldrich Chemistry with 20% wt in water. All aqueous solutions in the processes were prepared with deionized (DI) water supplied by a Barnstead nanopure Diamond-UV purification unit equipped with a UV source and a final 0.2  $\mu\text{m}$  filter. T K Filmics nanomixer (Model 56–50, PRIMIX Corporation, Japan) was used to perform the pretreatment. MILLEX syringe driven filter unit (0.22  $\mu\text{m}$ ) and Becton, Dickinson and Company BD 1 mL syringe with tuberculin slip tip were ordered from Fisher scientific. Glass microanalysis filter holder assembly was used for the filtration (Fisher scientific, PA) with filter papers (Grade 1, 11  $\mu\text{m}$ , D70 mm) from Whatman. Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA) and a refractive index detector were employed in the high performance liquid chromatography (HPLC) system for sugar analysis.

#### 2.1.1. Sample pretreatment

The corn stover samples were pretreated by the T K Filmics nanomixing reactor. The corn stover samples, 2 g of each, were mixed with 50 mL 0.4% and 4% w/v NaOH solutions at the mixing shear rate of 12500  $\text{s}^{-1}$  for 2 min with and without 10 mM and 60 mM PDAC based on the molecular weight of the polymer repeat unit (0.081 and 0.485 g in the mass weight), respectively. No external removal or addition of heat to the system was provided. The mixing temperature could reach up to 100 °C under ambient pressure without the addition of extra heating. After the 2 min mixing, cooling water was introduced until the system temperature was brought down to 25 °C. After the mixing, the pretreated samples were washed to neutrality with deionized water (DI) water, followed by filtration to get rid of most of water. Washed solids were spread evenly on the aluminum foil and air-dried for 2 days. Moisture content was measured based on oven-dried method. Another set of experiment was performed by adding 10 mM PDAC after pretreatment and stirring the mixed solution at room temperature for 5 min for complete mixing. The rest steps of washing, neutralization, and drying were kept the same.

#### 2.1.2. Enzymatic hydrolysis

The pretreated samples were enzymatically hydrolyzed using Accellerase 1000 (Danisco US Inc. Genencor Div., NY). Pretreated corn stover samples were immersed in pH 4.8 citrate buffer solution, and then incubated in water bath shaker at 150 rpm, 50 °C up to 168 h. The procedure and calculations were performed as NREL Laboratory Analytical Procedure (LAP) 013 (Selig et al.,

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