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Boosting the fermentable sugar yield and concentration of corn stover by magnesium oxide pretreatment for ethanol production

Jun Li[a], Wentao Li[a], Meng Zhang[b], Donghai Wang[a,*]

[a] Department of Biological and Agricultural Engineering, Kansas State University, Manhattan, KS 66506, USA
[b] Department of Industrial and Manufacturing Systems Engineering, Kansas State University, Manhattan, KS 66506, USA

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ABSTRACT

MgO pretreatment was investigated to boost the fermentable sugars derived from corn stover with LHW pretreatment as control. Compared to LHW pretreatment, MgO pretreatment caused twice hemicellulose recovery (42 vs 21%). Double hemicellulose recovery not only didn't affect glucose yield but increased xylose yield by 13% and total sugar yield by 6% under the optimal conditions (pretreatment: 10% biomass loading, 0.1 mol/L MgO, 190 °C, and 40 min; hydrolysis: pretreated biomass loading of 10 g/100 mL, enzyme loading of 1 mL/g pretreated biomass, 50 °C, and 120 h). A total sugar concentration of 50 g/L was obtained under the above conditions. Besides, the enzyme component hydrolyzing xylan may be prone to deactivation by lignin residues in pretreated biomass. Both SEM and FTIR analyses indicate that MgO effectively disrupted the biomass structures and enlarged the exposed surface area of carbohydrates, thus boosting the enzymatic hydrolysis and fermentable sugars for ethanol production.

1. Introduction

Bioethanol is regarded as a green, environmentally-friendly, and renewable biofuel and can be used to replace the unsustainable gasoline derived from fossil fuels (John et al., 2011). Starchy crops, such as grain sorghum, wheat, and corn, are usually considered as the most ideal biomass for bioethanol production owing to the high starch-to-ethanol conversion. The techniques for starch ethanol production have also been quite mature (Xu and Wang, 2017). However, overuse of starchy grains for ethanol production will compete with food and feed production (Xu et al., 2011). The increase in population and the increase in demand for animal feed are also intensifying the competition. Seeking new pathways to overcome this issue is a focus research topic. Lignocellulosic biomass is a great option to replace grains for ethanol production and has been attracting more and more attention (Demirbas, 2001; Hamelinck et al., 2005). Research results, however, have shown that the complex nature of its chemical structures endues lignocellulosic biomass a strong recalcitrance against the access of enzymes to carbohydrates, thus presenting a low enzymatic hydrolysis efficiency with a glucose yield of approximately 20% when taking conventional procedures (saccharification and fermentation) used to produce starch ethanol (Mosier et al., 2005). To improve the utilization efficiency of cellulosic biomass in cellulosic ethanol manufacturing, pretreatment is usually taken to untie the structural seal and improve the exposed surface area of carbohydrates so that the contact of enzymes with carbohydrates will increase (Choi et al., 2013).

Lots of biomass pretreatment methods have been explored such as alkali, acid, liquid hot water, organic solvent, ionic liquid, ammonia fibre explosion, physical assistance etc. (Chundawat et al., 2007; Kim et al., 2016; Lee et al., 2009; Liu et al., 2012; Timung et al., 2015; Yat et al., 2008; Zhang et al., 2016; Zheng et al., 2009), among which dilute sulfuric acid method has been industrialized (Zheng et al., 2013) and liquid hot water (LHW) method has also been attracting much attention owing to no chemical addition in the pretreatment step (Kim et al., 2015). However, both methods will cause a large amount of sugar degradation and inhibitor formation owing to the existence of acids (added sulfuric acid and released acetic acid). Sugar loss and inhibitor formation caused by acids will seriously affect the carbohydrate-to-sugar and sugar-to-ethanol conversions (Li et al., 2017; Pandey et al., 2014). The findings from our previous study (Li et al., 2018) have indicated that magnesium oxide (MgO) is an effective additive and can completely neutralize the acetic acid released from hemicellulose, thus leaving the biomass slurry nearly neutral and without furfural and HMF formation. Compared to LHW, the addition of MgO not only increases the cellulose recovery also the removal rate of lignin (Table 1), which is the major obstacle restricting the access of enzymes to carbohydrates and causing enzyme deactivation (Zhai et al., 2018). Moreover, the addition of MgO results in twice the amount of hemicellulose residues

* Corresponding author.
E-mail address: dwang@ksu.edu (D. Wang).

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Table 1
Composition analysis of treated and untreated CS.[1]

CS	Cellulose (%, db[4])	Hemicellulose (%, db[4])	Lignin (%, db[4])	Potential sugar recovery (%, db[4])		Lignin removal (%, db[4])	O/C ratio
				Glucose	Xylose		
Untreated	30.6 ± 0.34a[5]	24.0 ± 0.24a	15.6 ± 0.17a				0.34 ± 0.05a
MgO-treated[2]	45.7 ± 0.73b	15.1 ± 0.19b	22.7 ± 0.21b	90.1 ± 1.15a	41.5 ± 0.71a	22.8 ± 0.34a	0.27 ± 0.05b
LHW-treated[3]	46.7 ± 0.81b	8.3 ± 0.07b	27.1 ± 0.05c	84.4 ± 1.62b	20.7 ± 0.15b	16.8 ± 0.02b	0.25 ± 0.09c

[1] Data are present in mean plus and minus standard deviation.
[2] MgO pretreatment condition was 10% solid loading, 0.10 mol/L MgO, pretreatment temperature of 190 °C, and 40 min (Li et al., 2018).
[3] LHW pretreatment condition was 10% solid loading, pretreatment temperature of 190 °C, and 40 min (Li et al., 2018).
[4] db = dry basis.
[5] In each column, means with different letters are significantly different at $p < 0.05$.

in pretreated biomass (Table 1), which would increase the fermentable sugars.

The improvement in sugar recovery during MgO pretreatment increases the amount of initial sugars used for enzymatic hydrolysis, but does not warrant an increase in sugar yield during enzymatic hydrolysis. This is because sugar yield is determined by both the amount of initial sugars used for enzymatic hydrolysis (recovered sugars from pretreatment) and the sugar conversion during enzymatic hydrolysis (Eq. (1)). The degree of disruption to biomass microstructures by pretreatment decides the access of enzymes to carbohydrates, eventually determining the sugar conversion (Liu et al., 2009). Therefore, the effectiveness and feasibility of MgO pretreatment on boosting the enzymatic hydrolysis of cellulose-to-glucose and hemicellulose-to-xylose should be investigated as presented in Fig. 1. In order to accomplish this, the enzymatic hydrolysis efficiencies of MgO-treated corn stover (CS) were evaluated by comparing the yields and conversions of sugars (glucose, xylose, and total). The macro- and microstructural changes of CS during pretreatment were also assessed by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

$$\text{Sugar yield} = \frac{\text{sugar recovery from pretretament} \times \text{sugar conversion during enzymatic hydrolysis}}{\text{the amount of initial sugars in biomass used for pretreatment}} \times 100\% \quad (1)$$

2. Material and methods

2.1. Materials

MgO with a purity of > 96.0% was obtained from Fisher (Ward Hill, MA). Accellerase 1500 was freely supplied by DuPont Industrial Biosciences (Rochester, NY) with a endoglucanase activity of 2200–2800 CMC U/g and a β-glucosidase activity of 450–775 pNPG U/g. CS was collected from the Agricultural Trial Base (Kansas State

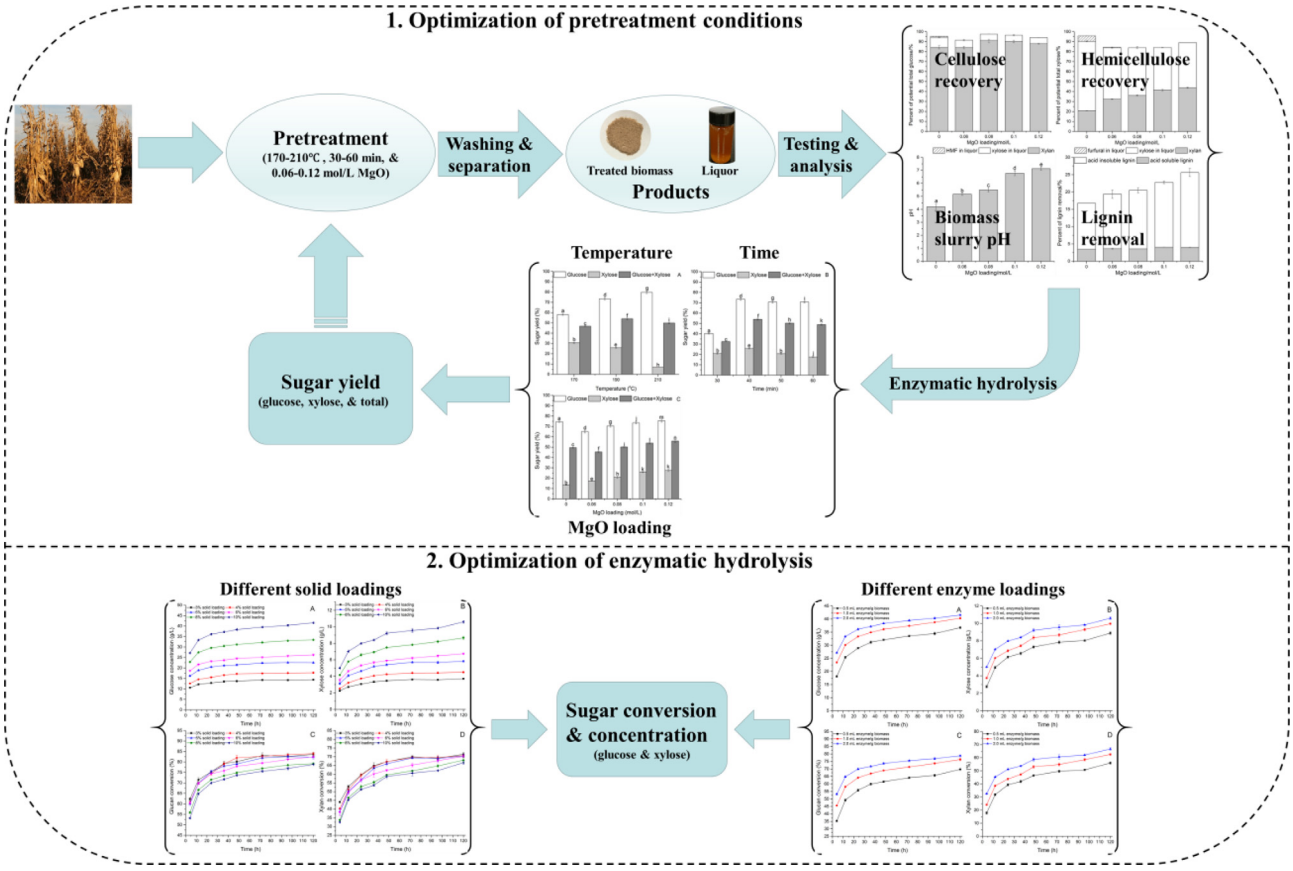

Fig. 1. The process flow diagram of this study.