Industrial Crops and Products 80 (2016) 86–92

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Enhancement of lignosulfonate-based polyoxyethylene ether on enzymatic hydrolysis of lignocelluloses

Xuliang Lin[a], Xueqing Qiu[a,b,*], Hongming Lou[a,b,*], Zihao Li[a], Ningxin Zhan[a], Jinhao Huang[a], Yuxia Pang[a]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China
[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China

ARTICLE INFO

Article history:
Received 21 July 2015
Received in revised form
18 September 2015
Accepted 8 November 2015
Available online 6 December 2015

Keywords:
Lignosulfonate-based polyoxyethylene ether
PEG
Hydrophilicity
Enzymatic hydrolysis
Corn stover
CTAB

ABSTRACT

Effect of the molecular structure of lignosulfonate-based polyoxyethylene ether (LS-PEG) on the enzymatic hydrolysis of Avicel and corn stover was investigated. With the increase of PEG contents and M_w of LS-PEG, glucose yield of corn stover increased from 16.7% to 51.9%. When LS-PEG was compounded with cationic surfactant cetyltrimethylammonium bromide (CTAB), the enhancement of glucose yield of corn stover was further increased from 45.3% to 62.8%. Sulfonic group of LS-PEG preferentially interacted with quaternary ammonium group of CTAB by the electrostatic attraction to form a similar non-ionic surfactant CTAB-LS-PEG. CTAB-LS-PEG showed electrically neutral and more hydrophobic, and blocked more nonproductive adsorption of cellulase on the lignin. Therefore, CTAB-LS-PEG enhanced enzymatic hydrolysis efficiency of lignocelluloses more significantly. The understanding developed in this study can help to develop potential approaches and strategies for effective application of lignosulfonate to improve bioconversion of lignocellulosic biomass.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Lignocellulosic biomass is the most abundant and renewable source on earth, and attracts an increasing attention. Lignocelluloses comprise three major components: cellulose (40–45%), hemicellulose (30–35%), and lignin (25–30%) (Xu et al., 2014). Cellulose and hemicellulose can be converted to value-add chemicals or bio-fuels through the sugar platform (Himmel et al., 2007; Ragauskas et al., 2006). Enzymatic hydrolysis process of lignocelluloses to sugar is the most promising for its high yield, high selectivity and mild operation. However, cellulase enzyme is still high cost, making cellulosic ethanol difficult to produce commercially. Furthermore, a pretreatment to alter and/or remove lignin and hemicellulose is necessary prior to enzymatic hydrolysis because of the recalcitrance of lignocelluloses (Zhao et al., 2012). The cost of the complete delignification in the pretreatment process of lignocelluloses is extremely high (Leu and Zhu, 2013). Thereby, the residual lignin would act as a physical barrier and an attractant to cellulase to reduce the adsorption of cellulase on cellulose (Kumar et al., 2012; Tu et al., 2009). Hence, lignin has a significant negative impact on the enzymatic hydrolysis of lignocelluloses (Li et al., 2014; Selig et al., 2007; Sewalt et al., 1997; Yao et al., 2012).

Hydrophobic interaction has been identified as the main driving force for nonproductive adsorption of cellulase on the lignin (Berlin et al., 2005; Sammond et al., 2014). Improving the hydrophilicity of lignin by carboxyl and sulfonation modification in the pretreatment process results in enhancing enzymatic hydrolysis of lignocelluloses (Del Rio et al., 2011; Nakagame et al., 2011). Acidic sulfite pretreatment to overcome recalcitrance of lignocelluloses can remove most of hemicellulose and dissolve lignin by sulfonation modification (Zhou et al., 2013b; Zhu et al., 2009). Acidic sulfite pretreated lignocelluloses can be used directly for enzymatic hydrolysis and fermentation without washing and detoxification, ethanol concentration can achieve 42 g/L and its theoretical yield can be 70% at a low cellulase loading (Zhang et al., 2015; Zhu et al., 2015). What's more, lignosulfonate (LS), a byproduct of acidic sulfite pretreated liquid of hard wood, performs better than the commercial LS from sulfite pulping in the enzymatic hydrolysis process (Zhou et al., 2013b; Zhu et al., 2015). Moreover, the hydrophilicity and charge of LS have a significant impact on the enzymatic hydrolysis efficiency of lignocelluloses (Lou et al., 2014a,b). LS with large molecular weight (M_w) and low degree of sulfonation showed poor hydrophilicity, adsorbed cellulase

* Corresponding authors at: School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China. Fax: +86 20 87114721.
E-mail addresses: xueqingqiu66@163.com (X. Qiu), cehmlou@scut.edu.cn (H. Lou).

http://dx.doi.org/10.1016/j.indcrop.2015.11.024
0926-6690/© 2015 Elsevier B.V. All rights reserved.

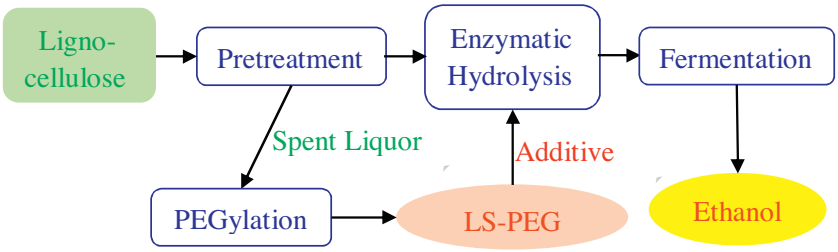

Fig. 1. Potential approaches and strategies for effective application of LS to improve bioconversion of lignocellulosic biomass.

nonproductively and restrained enzymatic hydrolysis of lignocelluloses (Wang et al., 2013a; Zhou et al., 2013a). While LS with high degree of sulfonation showed obvious negative charge, would reduce the enzymatic activity of cellulase and restrain enzymatic hydrolysis of lignocelluloses (Lou et al., 2014b; Wang et al., 2013b).

Polyethylene glycol (PEG) based non-ionic surfactants have proven to be the most effective in the enzymatic hydrolysis of lignocelluloses (Eriksson et al., 2002). Recently, lignin-based polyoxyethylene ether, prepared from enzymatic hydrolysis lignin and PEG, could significantly reduce nonproductive adsorption of cellulase on lignin and enhance the enzymatic hydrolysis of lignocelluloses by dispersing cellulase aggregates, was reported in our previous work (Lin et al., 2015a,b). This study is focused on the understanding of the application of LS-PEG on the enzymatic hydrolysis of lignocelluloses. The objectives are: (1) to investigate the effect of LS-PEG structures, i.e., PEG chain lengths, PEG contents, and M_w on the enzymatic hydrolysis of Avicel and corn stover; (2) to further enhance the enzymatic hydrolysis of lignocelluloses in the presence of LS-PEG with cationic surfactant by adjusting the charge and hydrophilicity. The understanding developed in this study can help to develop potential approaches and strategies for effective application of LS to improve bioconversion of lignocellulosic biomass, as shown in Fig. 1.

2. Materials and methods

2.1. Materials

Corn stover (CS) prepared by steam explosion pretreatment at 180 °C for 5 min was provided by Henan Tianguan Group Co., Ltd. (Nanyang, China). Corn stover was treated at 121 °C for 1 h by autoclave for sterilization to reduce the growth of bacteria, then was washed and dried at 50 °C for 48 h prior to enzymatic hydrolysis. The content of cellulose, acid-insoluble lignin, xylan and ash of the obtained corn stover was 30.8%, 27.6%, 14.2% and 22.1%, respectively.

LS is a byproduct of the sulfite pulping process of poplar wood from Shixian Papermaking Co., Ltd. (Jilin, China). The sulfonation degree of LS is 2.1 mmol/g and the phenolic hydroxyl content is 2.2 mmol/g.

Commercial cellulase enzyme Cellic CTec2 (abbreviated CTec2) derived from the fungus *Trichodermareesei* (*Hypocreajecorina*) was provided by Novozyme China (Shanghai, China). The protein concentration of cellulase is 73.6 mg/mL and its cellulase activity is 147 FPU/mL according to the literature method (Wood and Bhat, 1988).

Cotton linters Avicel (PH101) with a mean particle size of 50 μm, which was used as the pure cellulose, and PEGs with various M_w were purchased from Sigma–Aldrich (Shanghai, China). Cetyltrimethylammonium bromide (CTAB) was supplied by Aladdin (Shanghai, China). All chemicals were of analytical grade and used as received. Milli-Q water was used for the preparation of all solutions.

2.2. Synthesis of LS-PEG

LS-PEG was synthesized from LS and PEG in the alkaline solution according to our previous work (Lin et al., 2014). PEG was functionalized preferentially with epichlorohydrin using BF_3-Et_2O as Lewis acid catalyst at 55 °C for 2 h and then was grafted onto LS in the alkaline solution of pH 13 at 80 °C for 3 h. LS-PEG product was adjusted to the neutral by hydrochloric acid, then was extracted by butanone to remove unreacted PEG and purified LS-PEG was obtained. A series of LS-PEG with various PEG chain lengths, PEG contents and M_w was prepared by controlling the mass ratio of PEG to LS and the molar ratio of epichlorohydrin to PEG. The PEG content in the LS-PEG copolymer was measured indirectly through the UV spectrophotometric method. The M_w of LS-PEG was determined by the aqueous size-exclusion chromatography using sodium polystyrene sulfonate standards. PEG content, M_w and polydispersity index of LS-PEG are listed in Table 1.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis of cellulosic substrate was conducted at 2% (w/v) in 50 mL of pH 4.80, 50 mM acetate buffer in a shaker (DDHZ-300, Jiangsu Taicang equipment factory, China) at 50 °C and 200 rpm. LS-PEG or PEG was firstly added to the mixtures of the substrate and acetate buffer, and then 0.1 g/L of tetracycline was added to retard bacterial growth before adding cellulase. The cellulase loading was 5 FPU/g glucan. Aliquots of 1 mL were taken periodically (3, 6, 12, 24, 48, and 72 h) for glucose determinations after centrifuging at a centrifugal acceleration of 7379 g for 10 min. For fast analysis, glucose in the enzymatic hydrolysate was measured in duplicate using a commercial glucose analyzer (SBA-40E biosensor, Institute of Biology of the Shandong Academy of Sciences, China). Glucose yield, defined as the molar percentage of released glucose based on the glucose residue in the substrate, was used to represent the enzymatic hydrolysis efficiency of the substrate. Glucose yield was calculated according to the following equation:

$$\text{glucose yield} = \frac{0.9 \times \text{glucose}}{(\text{initial cellulose})} \times 100\%.$$

Control experiments without additives were also carried out for comparison. While control experiment with LS-PEG but no substrate was conducted, no released glucose was detected. The average of two replicates and their errors were shown in the figures.

3. Results and discussion

3.1. Effect of the molecular structure of LS-PEG on enzymatic hydrolysis of Avicel and corn stover

3.1.1. Effect of the concentration of LS-PEG on enzymatic hydrolysis of corn stover

LS at low dosage would restrain enzymatic hydrolysis of cellulose and enhance with increasing dosage (Zhou et al., 2013a). Therefore, effect of the concentration of LS and LS-PEG on the glu-

Download English Version:

https://daneshyari.com/en/article/4512589

Download Persian Version:

https://daneshyari.com/article/4512589

Daneshyari.com