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Multivariate data analysis applied in alkali-based pretreatment of corn stover

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ABSTRACT

In this paper, variables of Pulp Refining Instrument (PFI) refining assisted alkaline pretreatment and hydrolysis saccharification of corn stover were analyzed. The process parameters were characterized by multivariate data analysis methods including Principle Component Analysis and Partial Least Square (PCA and PLS) to investigate the specific relationships of primary variables in alkali-based pretreatment of biomass. In this paper, pretreatment system was multivariate and the variables were inter-related to each other. Total alkaline charge and removal rate of lignin had greatest impact on the pretreatment and enzymatic hydrolysis.

1. Introduction

In view of the shortage of fossil fuels and the worsening environmental problems all over the world, more researchers have focused on developing of sustainable bio-energy alternatives (Bichraoui-Draper et al., 2015; Ayamga et al., 2015). Bio-energy was one of the sustainable energy alternatives (Ding et al., 2012; Yang et al., 2013; Von Schenck et al., 2013; Sun and Cheng, 2002). During the bio-energy conversion process, enzymatic saccharification is one of the key steps to produce fermentable sugars, which can be further converted to bio-fuels (such as bio-ethanol) (Yu et al., 2013). The lignocellulosic biomass was considered as the most promising feedstock of the second-generation bio-ethanol (Ljungqvist et al., 2005). Main components of lignocellulosic biomass were polysaccharide (cellulose and hemicellulose) and lignin (Zhu et al., 2009; Khoo et al., 2015). As polysaccharide, cellulose and hemicellulose could be degraded to monosaccharide (fermentable sugars), which could be converted into bio-ethanol (Himmel et al., 2007; Luo et al., 2011).

However, the recalcitrance of lignocellulosic biomass, such as distribution and structure of lignin, was the bottleneck for the lignocelluloses energy conversion (Van Dyk and Pletschke, 2012). Thus, the pretreatment was considered as the key process to break the natural barriers of lignocellulosic biomass (Segal et al., 1959; Luo and Zhu, 2011). High efficient pretreatment could reduce the subsequent operating cost of the bioenergy conversion. There were many different biomass pretreatment categories (Oh et al., 2005), such as physical pretreatment, biological pretreatment, chemical pretreatment, and physicochemical pretreatment (Liu et al., 2013). Therein, the physicochemical pretreatment was considered as one of the high efficiency pretreatment to improve the enzymatic saccharification (Agbor et al., 2011). Enzymatic saccharification was normally produced by enzymatic hydrolysis process, in which polysaccharide could be decomposed into fermentable sugar by enzyme (e.g. cellulose, glucosidase).

Many different process variables were in the physicochemical pretreatment and enzymatic hydrolysis (Miura et al., 2012). More or less, these variables were associated with each other. In consideration of the relationship between the different variables (Li et al., 2011), studies of the pretreatment conditions, mechanical treatment, composition of pretreated corn stover, enzymatic hydrolysis effect could have an important guiding significance.

When multiple variables were involved, the data could be analyzed by a comprehensive dimension reduction method, which could summarize the main aspects or information of a dataset (Lin et al., 2015). The multivariate data analysis (PCA and PLS) were especially useful for reducing high-dimension multivariate systems

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(Godoy et al., 2014). On account of multiple linear regressions, the orthogonal transformation could be used by PCA method to transform the possibly correlated variables base set into a new base set of linearly uncorrelated variables (principal components). By PCA analysis, the variables could keep independent, and the data noise could be removed to help find the key variables for subsequent analysis. As a statistical method, PLS could reveal the relationship of principal components regression. PLS method could not just give the hyperplanes of minimum variance (response vs independent variables). PCA and PLS could simplify the complex process or issues, and reveal the essence of the variables (Li et al., 2014).

In this paper, the lignocellulosic biomass corn stover was treated by physicochemical pretreatment (PFI refining assisted alkaline pretreatment) and enzymatic hydrolysis process. Variables of the pretreatment and enzymatic hydrolysis were analyzed by PCA and PLS method to find the inter-relationships between each other in order to guide the further research of lignocellulosic biomass conversion.

2. Materials and methods

2.1. Raw material and chemicals

Corn stover (lignocellulosic biomass raw material) was harvested in the October in 2014, from Pingdu, China. Firstly, corn stover was milled by a grinder. Then, the milled samples were screended to collect the corn stover with the target particle size (0.18–0.85 mm). After that, the samples were stored in a sealed bag at temperature for following research. (The moisture content and composition analysis were shown in supporting information Table.1).

Sodium hydroxide was bought from Sinopharm Chemical Reagent Co.Ltd. Cellulase (Celluclast 1.5L) and β-glucosidase (Novozyme 188) were supplied by the Sigma-Aldrich China Inc. All enzymes and chemicals were used without further purification.

2.2. Alkaline pretreatment of corn stover

The alkaline pretreatment was conducted in a cooking reactor (Mode PL1-00, Xianyang TEST Equipment Co., Ltd., Xianyang, China). Four small cooking seal pots (1 L) were in the cooking reactor. For every small cooking pot, 50 g oven dried raw biomass was added with alkaline chemicals at certain ratio of liquid to solid and certain temperature for certain holding time (The pretreatment conditions could be seen in supporting information Table.2). After alkaline pretreatment, the cooking seal pots were cooled down quickly. Then, the pretreated corn stover samples was treated to be neutral by washing with water in a 300 mesh bag. Finally, the pretreated corn stover samples were stored at 4 °C for further study.

2.3. Mechanical refining treatment

The corn stover samples with alkali-based pretreatment were experienced the mechanical refining treatment (PFI) by a refiner (model PL11-00, Xianyang TEST Equipment Co., Ltd., China). The revolution numbers (corn stover samples treated by PFI between the fixed disc and rotating disc) of the PFI treatment in this work were 4000. The oven dried weight of corn stover samples was 10 g. The corn stover solid content and water content of the pretreated samples in PFI treatment were 10% and 90%, respectively. The speed of the PFI mechanical refiner was 1400 rpm (0.24 mm refining gap).

2.4. Enzymatic hydrolysis

In the enzymatic hydrolysis process, the alkali-based pretreated biomass samples were conducted in a 25 mL bottle with sodium citrate buffer and 0.02% sodium azide (0.05 M, pH 4.8), at 50 °C for 48 h. The process was produced in a water bath shaker (90 rpm). For 1 g dry pretreated corn stover, the dosage of β-glucosidase was 5 IU/g and the celulase was 20 FPU. Then, the supernatant liquid after enzymatic hydrolysis was collected and placed in a sealed bag at −10 °C for following experiment.

2.5. Analysis methods

National Renewable Energy Laboratory (NREL) protocol (Sluiter et al., 2008) was used to test the chemical composition of corn stover. A high performance liquid chromatography (HPLC)(Model 1200, Agilent, USA) with a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) was used to determine the enzymatic hydrolyzate at 55 °C with 0.005 M sulfuric acid.

The evaluation equations were as follows:

$$R_{\text{solid}}(\%) = (\text{weight of pretreated sample(g)}/\text{untreated sample(g)}) \times 100\% \quad (1)$$

$$R_{\text{glucan/xylan}}(\%) = (R_{\text{solid}} \times D_{\text{glucan/xylan of pretreated corn stover}})/D_{\text{glucan/xylan of raw corn stover}} \times 100\% \quad (2)$$

$$R_{\text{delignification}}(\%) = 1-(R_{\text{solid}} \times D_{\text{lignin of pretreated corn stover}})/D_{\text{lignin of raw corn stover}} \times 100\% \quad (3)$$

$$E_{\text{glucan}}(\%) = (A_{\text{glucose in hydrolyzate}} \times 0.9/A_{\text{glucan in pretreated corn stover}}) \times 100\% \quad (4)$$

$$E_{\text{xylan}}(\%) = (A_{\text{xylose in hydrolyzate}} \times 0.88/A_{\text{xylan in pretreated corn stover}}) \times 100\% \quad (5)$$

R_{solid} was the recovery rate of solid, $R_{\text{glucan/xylan}}$ was the recovery rate of glucan or xylan, $R_{\text{delignification}}$ was the removal rate of lignin, E_{glucan} was the enzymatic hydrolysis percentage of glucan, E_{xylan} was the enzymatic hydrolysis percentage of xylan. A was the weight of sugar (g). D was the component content (wt.%).

2.6. PCA and PLS analysis

The data analysis for PCA model and PLS model was calculated by the SIMCA-P 12.0 (Soft Independent Modelling of Class Analogy, Umetrics).

3. Result and discussion

3.1. Principal component analysis of the whole process

In this paper, the multivariate data analysis included PCA and PLS methods. The PCA was known as analysis for principal component, which was designed to reduce the dimension in order to reduce many indicators into a few composite ones. To comprehensively and systematically analyze the problems, the relationship between multiple different factors should be considered. Commonly, these factors or indicators in multivariate statistical analysis were known as variable. Since each variable reflected some information of the research issue in some extent, and each variable had a certain correlation with each other, the statistics information reflected by all the variables was partly overlapped. In the