Available at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe

Evaluation and optimization of organosolv pretreatment using combined severity factors and response surface methodology

Chun Sheng Goh [a], Hui Teng Tan [a], Keat Teong Lee [a], Nicolas Brosse [b,*]

[a] School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

[b] Laboratoire d'Etude et de Recherche sur le Materiau Bois, Faculté des Sciences et Techniques, Nancy Université, Boulevard des Aiguillettes, F-54500 Vandoeuvre-lés-Nancy, France

ARTICLE INFO

Article history:
Received 7 March 2011
Received in revised form
6 June 2011
Accepted 17 June 2011
Available online 20 July 2011

Keywords:
Empty palm fruit bunches
Organosolv pretreatment
Combined severity
Central composite design
Optimization
Bioethanol

ABSTRACT

In this study, ethanol organosolv pretreatment was investigated and optimized for the pretreatment of empty palm fruit bunch using (1) response surface methodology based on three-variable central composite design and (2) the combined severity parameters. The reaction parameters studied were sulfuric acid concentration (0.5–2.0%), reaction temperature (160–200 °C) and residence time (45–90 min). Both models provide valuable and complementary informations: using combined severity parameters, very good predictions were obtained concerning xylan and lignin extraction whereas central composite design is the best model for glucose production. The optimal values of the variables were as the followings: sulfuric acid 2.0% w/w, 160 °C, 78 min and the experimental values (96.0%) concerning glucose and lignin recovery were in excellent agreement with the central composite design prediction (100%).

1. Introduction

Compared to first generation bio-ethanol, cellulosic ethanol does not compete with food [1]. Although pretreatments are required to alter the structure of the biomass, to break the lignin seal and disrupt the crystalline structure of cellulose. Various pretreatment methods have been developed to recover more glucose from lignocellulosic biomass, including steam explosion, sulfuric acid and organosolv treatments [2]. Pretreatment is one of the most expensive processing steps in cellulosic biomass-to-fermentable sugars conversion and a rigorous optimization of the conditions should be one of the major goals of optimizing a biomass-to-ethanol process to effectively reduce overall cost. A quality pretreatment should have the criteria of increases pulps digestibility and favors a high recovery of glucose from the biomass. However, interaction effects of process parameters have caused complexity and difficulties for the evaluation and optimization of the pretreatment. Regardless of the type of treatment, three major parameters were found to have significant effects are reaction temperature, residence time and lastly the amount of catalysts (e.g, steam explosion in a batch or continuous operation, autohydrolysis, or solvent delignification) [3–7]. Statistical approaches were often employed to investigate the optimum conditions for pretreatment processes [8–11]. Central Composite Design (CCD) and Response Surface Methodology

* *Corresponding author*. Tel.: +33 3 83 68 48 62; fax: +33 3 83 68 44 98.
E-mail address: nicolas.brosse@lermab.uhp-nancy.fr (N. Brosse).
0961-9534/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biombioe.2011.06.034

(RSM) were used to design a systematic experimental method. RSM is able to map a response surface over a particular region of interest. CCD is well suited for fitting a quadratic surface which usually works well for process optimization. For a CCD with three factors, the total number of runs amounts to 20, with center point having 6 replicates, which is significantly less than the amount of runs required for a full factorial design. It is able to produce a quadratic model by using five-level design [12]. However, not every types of response produce significant model with the factors. Therefore, in this case, the effectiveness of pretreatments was also evaluated using severity correlation which describes the severity of the pretreatment as a function of treatment time and temperature. The effect of the pH was taken into consideration through the combined severity (CS) parameters [13,14].

Organosolv ethanol pretreatment is a promising method to enhance the recovery of glucose by improving the digestibility of biomass. In addition, it produces high purity lignin which can be processed to other valuable products. Several organosolv pretreatment studies were carried out with miscanthus, pitch pine, wheat straw, olive tree trimmings and other lignocellulosic biomass [15–19]. Basically, this process separates the biomass into three major fractions: solid pulp which is rich in cellulose, liquid fraction which is rich in hemicellulose sugars and ethanol organosolv lignin (EOL) precipitated from liquid fraction.

As one of the world's largest palm oil producer, Malaysia produces a large quantity of oil palm residues. Among the residues, empty palm fruit bunch (EPFB) is produced as waste during harvest of fresh fruit bunch. In 2007, cultivations in Malaysia generated 6308 dry ktons of EPFB [10]. The high potential sugar content from cellulose and hemicelluloses in EPFB makes it a suitable low cost feedstock for the production of bio-ethanol. There are reports on the acid and hydrothermal pretreatment of other oil palm residues, however none of organosolv pretreatment as well as pretreatment of empty fruit bunches has been studied [20,21].

In this study, ethanol organosolv pretreatment conditions were investigated and optimized for the pretreatment of EFPB using (1) response surface methodology based on three-variable central composite design (CCD) and (2) the combined severity parameters. The two different approaches were evaluated as indicators of the effectiveness of the process in terms of overall glucose production (after enzymatic hydrolysis) and xylan and lignin recovery.

2. Materials and methods

2.1. Materials

EPFB was collected from oil palm cultivation in the Tali Air Estate (Sime Darby), Bagan Serai, Perak, Malaysia. It was washed rigorously with water and dried under the sun before it was sent by air mail to France. The empty fruit bunch was cut with knife into smaller pieces. It was milled into small pieces of fiber using a Wiley mill. All chemical reagents used in this study were purchased from VWR International and Aldrich and used as received. The enzymes were obtained from Sigma Aldrich (St. Louis, MO) and the K-EtOH ethanol measurement kit was obtained from Megazyme International (Bray, County Wicklow, Ireland). Total polyphenol content of EFB was gravimetrically determined as Klason lignin (32.2%) and as soluble lignins (2.6%) by UV quantification. The raw material also contains 42.6% of glucans, and 1.2% ash.

2.2. Organosolv pretreatment

A 1.0-L glass-lined pressure Parr reactor with a Parr 4842 temperature controller (Parr Instrument Company, Moline, IL) was employed for the pretreatment. Twenty grams of EPFB (dry mass) was treated with ethanol/water mixture in a volume ratio of 65:35 with sulfuric acid as a catalyst. The solid-to-liquid ratio used was 1:8. The mixture was stirred continuously and heated at a rate of ~3 °C/min. Depending on the experiment conditions, the pressure increased to 15–20 bars. After the desired residence time was reached, the pretreated biomass was washed three times with 150 mL of 60 °C ethanol–water in 8:2 ratio and air-dried overnight. EOL was precipitated out by adding three volumes of water to the combined washes. The washed and dried biomass, EOL, and a portion of the liquid were stored in a freezer at −5 °C before analysis.

2.3. Analytical procedures

Oven-dried weights were determined using a moisture analyzer (Mettler HR73). The biomass was then ground to pass a 40-mesh screen, according to the laboratory analytical procedure (LAP) provided by the National Renewable Energy Laboratory (NREL). Samples were hydrolyzed with 72% sulfuric acid for 1 h at 30 °C. After that, it was diluted to 3% sulfuric acid by adding water and then autoclaved at 121 °C. The dried residues obtained after filtration of autoclaved samples were weighed to give the Klason lignin content. Monosaccharide contents in the filtrate were quantified using an anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The acid-soluble lignin content was determined from absorbance at 205 nm according to Lin and Dence [22]. To determine the composition of the water-soluble fractions, an aliquot (10.00 mL) was freeze-dried and re-dissolved in deionized water (10.00 mL), and the monosaccharide contents were quantified using HPAEC-PAD before and after hydrolysis in order to determine the amount of oligomers. The latter was accomplished by addition of 72% H_2SO_4 to obtain a 3% sulfuric acid solution (348 μL). Furan contents were estimated in the first effluent (obtained through the sampling valve) and in the water-soluble fraction from the absorbance at 284 and 305 nm [7,18].

2.4. Enzymatic hydrolysis

The pulp (solid fraction) after organosolv treatment was separated from liquid through filtration. The remaining solid was washed with water and oven-dried at 45 °C. 1 g of the dry solid fraction was mixed with 50 mL of 0.05 M sodium acetate buffer (pH 4.8) in a 100 mL Erlenmeyer flask at 48 °C for 48 h. 15 IU/g biomass of β-glucosidase Novozym 188 and 15 FPU/g biomass of Celluclast 1.5 L were loaded into the slurry for enzymatic hydrolysis. The glucose content of the slurry after enzymatic hydrolysis was determined by HPLC in a Shimadzu liquid