Bioresource Technology 199 (2016) 121–127

Contents lists available at ScienceDirect

Bioresource Technology

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

Two-stage, acetic acid-aqueous ammonia, fractionation of empty fruit bunches for increased lignocellulosic biomass utilization

Dong Young Kim [a], Young Soo Kim [a], Tae Hyun Kim [b], Kyeong Keun Oh [a,*]

[a] Department of Applied Chemical Engineering, Dankook University, Cheonan, Chungnam 330-714, Republic of Korea
[b] Department of Environmental Engineering, Kongju National University, Cheonan, Chungnam 330-717, Republic of Korea

HIGHLIGHTS

- EFB was fractionated through two-stage fractionation.
- The used catalytic media are acetic acid and aqueous ammonia.
- No washing, no neutralization, and no corrosion.
- A little inhibitors from sugar degradation products were generated.
- Improved utilization of lignocellulosic biomass has been proposed.

ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 4 September 2015
Accepted 5 September 2015
Available online 21 September 2015

Keywords:
Weak acid
Weak alkali
Acetic acid hydrothermal (AAH)
Pretreatment
Enzymatic digestibility

ABSTRACT

Fractionation of EFB was conducted in two consecutive steps using a batch reaction system: hemicellulose hydrolysis using acetic acid (AA; 3.0–7.0 wt.%) at 170–190 °C for 10–20 min in the first stage, and lignin solubilization using ammonium hydroxide (5–20 wt.%) at 140–220 °C for 5–25 min in the second stage. The two-stage process effectively fractionated empty fruit bunches (EFB) in terms of hemicellulose hydrolysis (53.6%) and lignin removal (59.5%). After the two-stage treatment, the fractionated solid contained 65.3% glucan. Among three investigated process parameters, reaction temperature and ammonia concentration had greater impact on the delignification reaction in the second stage than reaction time. The two-stage fractionation processing improved the enzymatic digestibility to 72.9% with 15 FPU of cellulase/g of glucan supplemented with 70 pNPG of β-glycosidase (Novozyme 188)/g-glucan, which was significantly enhanced from the equivalent digestibility of 28.3% for untreated EFB and 45.7% for AAH-fractionated solid.

1. Introduction

Lignocellulosic biomass has been suggested as an abundant and promising source of bio-based fuels and chemicals, including various biofuels (e.g., ethanol, butanol and biogas), biopolymers, and various intermediate chemicals (Alvira et al., 2010). This lignocellulosic biomass is therefore a promising renewable feedstock for various biorefinery industries in the future since its three main constituents are cellulose, hemicellulose, and lignin (Huijgen et al., 2012; Snelders et al., 2014). These components can be used as precursors and intermediates for biofuels and value-added chemicals, which promise to make such a biorefinery process economically feasible. Efficient fractionation of lignocellulosic biomass into its three main constituents can improve overall efficiency in the biorefining industry. Therefore, lignocellulose will be more effectively and completely utilized by developing an effective fractionation method. On the other hand, lignin and hemicellulose have been reported as chemical and physical barriers, which serve as inhibitory compounds to the enzymatic hydrolysis of cellulose, and then further conversion to ethanol (Alvira et al., 2010). Therefore, removal of hemicelluloses and lignin in the fractionation process prior to converting cellulose to ethanol using enzymatic saccharification and microbial fermentation helps to avoid these problems. Previous research has mainly focused on finding efficient pretreatment methods to render the cellulose fraction in lignocellulosic biomass amenable to the action of cellulase enzymes.

In general, the various methods can be categorized according to their pHs (Avci et al., 2013). Commonly, acid pretreatment (low pH) method uses various types of acid to increase the hydrolytic reactivity. Alkaline pretreatment (high pH) typically uses either

* Corresponding author. Tel.: +82 41 550 3558; fax: +82 41 559 7867.
E-mail address: kkoh@dankook.ac.kr (K.K. Oh).

http://dx.doi.org/10.1016/j.biortech.2015.09.049
0960-8524/

sodium hydroxide or ammonia solution. Acid pretreatment cleaves the polymeric sugar chains, mainly in cellulose and hemicellulose. The liquid hydrolysate from acid treatment contains various compounds, including sugar degradation products (furfural and hydroxymethylfurfural (HMF)), organic acids, and phenolic compounds, which have been reported to be toxic to microorganism in the fermentation. Therefore, the formation of inhibitors should be monitored and minimized (Gu et al., 2014; Larsson et al., 1999; Palmqvist and Hahn-Hägerdal, 1999; Palmqvist and Hahn-Hägerdal, 2000). Alkaline pretreatment is effective for lignin solubilization; i.e., sodium or ammonium hydroxide breaks off the ether bonds in lignin polymers and both ether and ester bonds in lignin-carbohydrate complex. Recent efforts have focused on developing an effective and synergistic fractionation method combining two different pretreatment methods, such as hot-water + ammonia, steam explosion + sodium hydroxide, and steam explosion + organosolv (Alizadeh et al., 2005; Chen and Liu, 2007; Hendriks and Zeeman, 2009; Montane et al., 1998). Many studies have examined methods hydrolyzing hemicellulose prior to delignification-application of organosolv-steam treatments (Take et al., 2006), dilute acid soaking treatments (Brosse et al., 2009) and hydrothermal treatments (El Hage et al., 2010; Romaní et al., 2011).

In our previous work, acetic acid-assisted hydrothermal (AAH) fractionation was developed for effective hemicellulose recovery, mostly of xylan as xylo-oligomer, from empty fruit bunches (EFB). Acetic acid (AA) can provide a strong catalytic effect for the hydrolysis of XMG (xylose + mannose + galactose) with low by-products formation. According to our previous report, however, the AAH process resulted in relative low enzymatic digestibility (Kim et al., 2015).

In this study, therefore, we propose a two-stage fractionation method to recover hemicellulose using AA in the first stage and then to hydrolyze lignin using ammonium hydroxide in the second stage. The effects of three process variables, namely reaction temperature, reaction time, and catalyst concentration, are evaluated for maximum recovery of hemicellulose and delignification. In addition, hydrolysis of the fractionated solid is tested and its digestibility measured to evaluate the pretreatment effect of the two-stage fractionation method. The mass balance of EFB fractionation using two-stage method is also presented and reviewed.

2. Methods

2.1. Feedstock

EFB was obtained from a local palm oil processing company in Malaysia (Waris Selesa Sdn Bhd, Sabah, Malaysia) and stored in low-temperature drying at 45 °C in order to suppress the growth of contaminating cells and to prevent structural changes at higher temperature. The EFB was ground and screened to the nominal size of 7–14 mesh (1.4–2.38 mm) using a laboratory knife mill and US standard sieve. The moisture content of the ground EFB was determined to be 6.5% by oven method.

2.2. Experimental set-up and operation of two-stage process

The EFB was fractionated by two-stage method using a custom-made reactor system, which was designed and manufactured by SugarEn Co. Ltd. (Cheonan, Korea). The two-stage reactor system consists of one main tubular reactor, two chemical reservoirs, and one liquid sample receiver tank. The main reactor was equipped with a magnetic agitator, heating device, and bottom outlet valve with stainless steel screen wire mesh (Swagelok Company, cat #200-SS-316L). The internal volume of the main reactor is 1508 mL (length 275 mm length × 70 mm of internal diameter). Two chemical reservoirs contained two different catalytic solutions, which were introduced into the main reactor consecutively. Each reservoir had a heating device for preheating to the desired temperature, at which point, the chemical was added into the reactor. The temperature of the liquid sample holding tank was controlled to minimize sugar degradation in the liquid hydrolysate after fractionation operation. All reaction systems including, reactor, vessels, tubing, fittings, and valves, were constructed with SS-316L stainless steel. EFB was fractionated in two consecutive reaction steps: hemicellulose was hydrolyzed using AA in the first step, after which the lignin was solubilized using aqueous ammonia in the second step.

Both of the liquid catalysts, i.e., AA and aqueous ammonia, in the reservoirs were preheated until the desired temperature was attained in order to control the reaction temperature in the main reactor with biomass within 1 min. Fifty grams of EFB was loaded in the reactor, which was also preheated to a temperature of 45 ± 5 °C. For the first step, 450 mL of preheated AA was transferred quickly into the main reactor by opening the bottom outlet valve on the first vessel. After completion of the first stage reaction, the hydrolysate, containing soluble sugars, was separated from the remaining solid and recovered from the reactor using screen mesh and drained via the bottom outlet valve. The liquid product was then collected in the liquid sample receiver tank and quenched immediately. The solid residue after first-stage treatment was run through the second stage of the delignification reaction using aqueous ammonia with no washing, neutralizing, or drying. The second-stage run using aqueous ammonia was carried out following the same steps as in the first stage procedure. Preheated ammonia solution was introduced into the reactor with a solid/liquid ratio of 1/10 (w/v), which is oven dry basis. At reaction completion, the bottom outlet valve was opened to separate the liquid hydrolysate from the residual solid. The residual solid and liquid after two-stage fractionation were glucan-rich solid cake, xylan-rich liquid, and lignin-rich liquid, respectively. Fig. 1 shows the schematic illustration for the two-stage consecutive fractionation process on EFB using acetic acid and aqueous ammonia.

2.3. Analytical methods

The chemical compositions of the solid and liquid samples were determined following the procedures of the NREL (National Renewable Energy Laboratory, Golden, CO, USA) laboratory analytical procedures (LAP) (NREL/TP-510-42618 for structural carbohydrates and lignins; NREL/TP-510-42623 for sugars in the liquids or in the hydrolysates) (Sluiter et al., 2011; Sluiter et al., 2008). The sugars were determined using high performance liquid chromatography (HPLC; Breeze model, Waters Co., Milford, MA, USA) equipped with a refractive index (RI) detector (Waters 2414, Waters Co., Milford, MA, USA). A Bio-Rad Aminex HPX- 87H column (300 mm length × 7.8 mm internal diameter) and Cation H micro-guard cartridge (30 mm length × 4.6 mm internal diameter) (Bio-Rad Laboratories Inc., Hercules, CA, USA) were used for sugar analysis. The sample was filtered using a syringe filter (Whatman, 0.45 mm pore size, Fisher Scientific Cat #6779-1304) before analysis and the mobile phase was 5.0 mM sulfuric acid. The HPLC analysis conditions were a column temperature of 60 °C and a mobile phase flow rate of 0.6 mL/min. The conversion factors for dehydration of polymeric sugars to monomeric sugars were 0.9 (molecular weight ratio of glucan/glucose = 162/180) for glucan-to-glucose and 0.88 (=molecular weight ratio of pentosan/pentose = 132/150) for XMG (xylan + mannan + galactan) to XMG. The conversion factor for XMG ignores the factor for mannose and galactose, because xylose is the dominant sugar of the hemicellulose of EFB. The sugars in the liquid samples were determined after secondary acid