Fuel 203 (2017) 187–196

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Detoxification of hemicellulose-rich poplar hydrolysate by polymeric resins for improved ethanol fermentability

Yang Yu *, Lew P. Christopher

Biorefining Research Institute, Lakehead University, Thunder Bay, Ontario P7B 5E1, Canada

HIGHLIGHTS

- ASL removed effectively by both IRA-400 (OH^-) and XAD-4.
- Xylo-saccharides loss significantly reduced with IRA-400 (OH^-) treatment.
- Significant phenolics and HMF removal, poor acetic acid removal by IRA-400 (OH^-).
- Better fermentability with IRA-400 (OH^-) treatment prior to enzymatic hydrolysis.

ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form 20 April 2017
Accepted 26 April 2017
Available online 3 May 2017

Keywords:
Hemicellulose-rich hydrolysate
Detoxification
Synthetic polymeric resins
Inhibitor removal
Ethanol fermentability

ABSTRACT

Inhibitors generated during biomass pretreatment negatively affect fermentability of biomass hydrolysates and need to be removed prior to fermentation. In this study, four different polymeric resins were evaluated for their abilities to remove acid soluble lignin (ASL) from poplar hydrolysate. The ASL removal capabilities of Amberlite IRA-400 (OH^-) and XAD-4 were similar (96.7% and 97.3%, respectively), however 88% of xylo-saccharides (XS) were lost with XAD-4 treatment as compared to 21% with IRA-400 (OH^-) treatment. IRA-400 (OH^-) was also efficient in adsorption of aromatic-based inhibitors such as benzoic acid, vanillin and 4-hydroxybenzoic acid. The consecutive resin IRA-400 (OH^-) → enzyme (HTec2) treatment removed 79.5% of ASL from the hydrolysate at a loss of only 9.5% of xylo-based carbohydrates (XBC). This improved the hydrolysate fermentability to ethanol attaining 41.5 g/L ethanol titer and 89.6% ethanol yield at a sugar utilization efficiency of 95.3% after 72 h of fermentation.

1. Introduction

With the increasing demand for global energy and the unsustainable supply of fossil fuels, more research efforts are being invested in the development of green processes for the production of cellulosic biofuels. However, during pretreatment of the recalcitrant lignocellulosic biomass, toxic compounds are usually generated, such as phenolic compounds from lignin, furan derivatives (furfural and 5-hydroxymethyl furfural, 5-HMF) from carbohydrate dehydration, and aliphatic acids (acetic, formic and levulinic acids) from hemicellulose breakdown [1]. These compounds inhibit the enzymatic hydrolysis and fermentation and must be removed in order to increase the biofuel yield. The low molecular weight (LMW) phenolic compounds generated from the cleavage of ether linkages in lignin together with the secondary products of carbohydrate dehydration are systematically named acid soluble lignin (ASL) [2,3]. ASL is considered as one of the most potent inhibitors in ethanologenic fermentation [1,4]. Phenolic compounds disrupt cellular replication, sugar metabolism, cell membrane integrity of microorganisms [5,6], and inhibit activities of enzymes such as endo-glucanase and β-glucosidase [7–9].

A variety of physical, chemical and biological methods have been applied for removing inhibitors prior to enzymatic hydrolysis and fermentation. These include evaporation, overliming, activated carbon adsorption, solvent extraction, biological detoxification, etc. However, polymeric resins are regarded as one of the best ways to remove hydrolysate inhibitors [10]. Polymeric resins are mechanically and chemically stable, have high adsorption capacity, and can be regenerated under mild conditions [11]. They have been widely used for removal of phenolic compounds in wastewater treatment

Abbreviations: ASL, acid soluble lignin; DVB, divinylbenzene; HMF, hydroxymethyl furfural; XS, xylo-saccharides, including xylooligosaccharides and xylopolysaccharides; XBC, xylo-based carbohydrates, including xylose and XS.

* Corresponding author at: Biorefining Research Institute, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada.
E-mail address: yyu4@lakeheadu.ca (Y. Yu).

http://dx.doi.org/10.1016/j.fuel.2017.04.118
0016-2361/

[12]. Among them, anion-exchange resins and non-polar adsorbents have demonstrated strong adsorptive capacities [11]. Recently, with the development of bio-based fuels and chemicals, polymeric resins are increasingly researched for their use in detoxification of biomass-derived hydrolysates [13–15]. Anion-exchange resins have shown capacity for removing inhibitors, such as phenolic compounds, furan derivatives and aliphatic acids [13]. For instance, the styrene/DVB-based strong anion-exchange resin AG1-X8 removed 91% of phenolic compounds present in spruce hydrolysate [16], whereas 62% of phenolic compounds were removed from sugarcane bagasse hydrolysate via a series of treatments with anion and cation exchange resins [17]. In a comparative study of spruce hydrolysate detoxification, strong anion resins demonstrated a greater detoxification capacity than non-polar and cation resins, which resulted in ethanol production at higher titers and yields [13]. The non-polar XAD-4 adsorbent is another polymeric resin that is effective in inhibitor removal from lignocellulosic hydrolysates [18–20]. Using XAD-4, 90% of ASL was removed from a hardwood hydrolysate that allowed bioethanol yield to reach 97% of the theoretical maximum in a fermentation process with a genetically-modified ethanologenic *Escherichia coli* K011 strain [21]. The adsorptive capacity of ion-exchange resins is mostly attributed to the presence of hydrogen bonds, whereas the hydrophobicity, high surface area and macroreticular structure are believed to be the responsible factors for the non-polar XAD-4 adsorption effectiveness [18,22].

To date, only a few studies have systematically investigated polymeric resins for their abilities to remove inhibitors from lignocellulosic hydrolysates. The aim of this work was to evaluate four Amberlite® polymeric resins, XAD-4, IRA-958 (Cl^-), IRA-400 (Cl^-) and IRA-400 (OH^-), for their efficiencies in removal of ASL and abilities to retain xylose-based carbohydrates (XBC) in a hemicellulose-rich poplar hydrolysate. Another objective of this study was to examine the adsorption performance of these resins and gain a better understanding of the mechanisms involved therein. While quantifying phenolic compounds in wood hydrolysates was a challenging task [1], we used ASL as an indicator for the removal efficiency of polymeric resins. The retention/loss of xylosaccharides (XS) during the resin treatment of the hydrolysate was taken into account when comparing the resin performance. To our knowledge, this is the first report that provides a comprehensive study of polymeric resins with different matrices (styrene vs acrylate), functional groups (non-polar vs strong anion) and counter-ions (OH^- vs Cl^-) for their usefulness in detoxification of wood hydrolysates.

2. Material and methods

2.1. Poplar hydrolysate

Poplar wood chips (8 kg) were soaked in water at 1:4 ratio (w/v) overnight and then drained through a sieve of mesh size 4# (pore/opening size of 4750 μm). The soaked chips were then loaded into a custom-made pressurized percolation reactor and pre-steamed at 100 °C for 60 min, followed by cooking with saturated steam at 170 °C for 120 min. To adjust temperature, the purging steam was frequently discharged from the reactor, condensed and collected (liquid purge). At end of the cooking, the pressure of the reactor was instantly released to atmosphere through a discharge valve, which caused fibrillation of the wood chips. The fiber-like biomass was then pressed in a custom-made hydraulic press cylinder at 3000 psi through a sieve of mesh size 80# (pore/opening size of 180 μm) for 25 min until the liquid (C5 liquor) in biomass was completely drained. The liquid purge and C5 liquor were combined and vacuum-concentrated about 4 times at −70 kPa and 50 °C. The pH of the concentrated hydrolysate was in the range 3.5–4.0.

2.2. Resin properties and preparation

Four polymeric resins were studied for their detoxification potential on poplar hydrolysate. Three of them, XAD-4, IRA-400 (Cl^-) and IRA-400 (OH^-), had the same matrix of polystyrene crosslinked with divinylbenzene (DVB), while IRA 958 (Cl^-) was composed of a polyacrylate matrix crosslinked with DVB. XAD-4 is a non-polar hydrophobic adsorbent whereas IRA-400 (Cl^-) and (OH^-) are strong anion-exchange resins containing tertiary amine functional groups. IRA-958 (Cl^-) is also a strong anion-exchange resin containing tertiary amine functional groups with a polyacrylate/DVB matrix that confers a polar and hydrophilic nature [12]. The resin characteristics are presented in Table 1.

All resins were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Before use, the (OH^-) and (Cl^-) resin forms were soaked overnight in a solution containing 10% (w/v) NaOH and 10% (w/v) NaCl solution at a 1:2 resin to liquid ratio (w/v). The non-polar adsorbent XAD-4 was soaked in 100% methanol at a 1:2 resin to methanol ratio (w/v) overnight. The resins were washed with excess amount of deionized water, vacuum-dried to 50% water content (resin to water ratio of 1:1), and kept at 4 °C until use.

2.3. Determination of ASL concentration

The ASL concentration was determined using a procedure described by Schwartz and Lawoko [21]. ASL was diluted to a desired concentration that corresponded to an absorbance reading between 0.2 and 0.7 at 205 nm wavelength determined by a UV–visible spectrophotometer (Varian Cary 50Bio, Varian Inc., Palo Alto, California, USA) with 1 cm path length. The ASL concentration (in g/L) was calculated using Eq. (1):

$$ASL\ (g/L) = (A_{205} \times f)/(a \times l) \quad (1)$$

where

A_{205}: Absorbance at 205 nm
f: Dilution factor
l: Path length (1 cm)
a: Absorptivity, 113 L/g-cm for hardwood extracts

2.4. Determination of sugars, organic acids, furan derivatives and ethanol concentrations

The concentrations of sugars, organic acids, furan derivatives and ethanol were determined using HPLC (1260 Infinity, Agilent Technologies, Santa Clara, CA, USA) equipped with a refractive index detector (RID) and an Aminex HPX-87H column (Bio-Rad, Hercules, California, USA). The mobile phase was 5 mM H_2SO_4 and the flow rate was 0.5 mL/min. The temperature of the column and detector was maintained at 60 °C and 35 °C, respectively. The sample was filtrated through a 0.2 μm syringe filter before applying to HPLC.

2.5. Determination of XS concentration

The XS concentrations were determined following a modified NREL protocol for determination of sugars [23]. 5 mL of the hydrolysate was added to a pre-weighed glass tube, followed by adding 72% H_2SO_4 to a final concentration of 4% H_2SO_4. The glass tube was sealed and weighed before autoclaving at 121 °C for 1 h. After cooling to room temperature, the tube was weighed again and the loss of water during autoclaving was compensated by adding deionized water. The xylose concentration following acid hydrolysis was