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Improved enzyme efficiency of rapeseed straw through the two-stage fractionation process using sodium hydroxide and sulfuric acid

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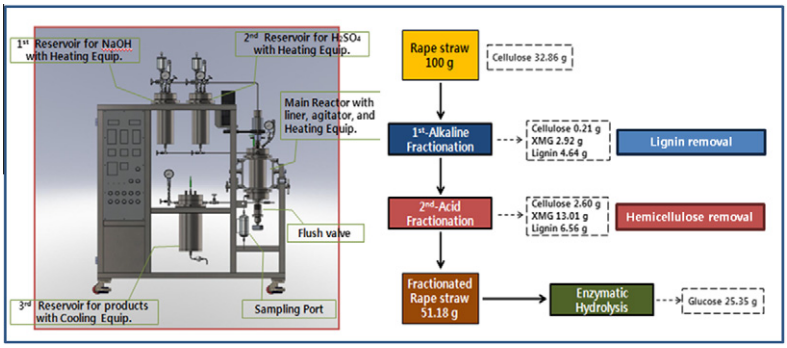
HIGHLIGHTS

- Two-stage fractionation for removing lignin and XMG from biomass performed.
- Evaluation of lignin removal conducted by changes in relative sugar content because of its ambiguities.
- High fractionation yield could be achieved with very low sugar decompositions.
- Higher digestibility was obtained for fractionated straw comparing to for acid pretreated straw.

GRAPHICAL ABSTRACT



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ABSTRACT

Two-stage fractionation process using sodium hydroxide and sulfuric acid was conducted to remove lignin and hemicellulose from rapeseed (*Brassica napus*) straw. This process consists of two stages; using sodium hydroxide, the first stage solubilized 35.54% of lignin and increased the glucan content in the treated solid from 32.86% to 38.13%. The second stage solubilized 85.85% of the lignin and 91.56% of the XMG (Xylan + Mannan + Galactan) into hydrolyzate. After the two-stage process, merely 2.53% of glucan and 3.81% of XMG were lost due to excessive decomposition. Despite the reduction in enzyme loading by 50%, the enzymatic digestibility with the two-stage treated straw was approximately 23% higher than that of the single stage acid fractionation process.

1. Introduction

Much attention has been drawn to renewable carbohydrate energy sources due to global issues such as the shortage of fossil fuel and environmental changes caused by rapidly increasing energy demand [1–3]. Biofuels, such as cellulosic ethanol, can be produced from lignocellulosic biomass generated from plant resources including agricultural and forest wastes [4]. Main components of lignocellulosic biomass include cellulose, hemicellulose, and lignin. The cellulose can be used as a resource for bioethanol production through enzymatic hydrolysis and fermentation [5–7]. The advanced agroindustrial byproducts are renewable, widespread, and generally an inexpensive source of biomass. Rapeseed straw is a disposal residue generated from the bio-oil industry in Korea. An adequate use of the rapeseed straw will give an added value for this material and a solution for the removal of this abundant waste, solving an energy crisis, and increasing the economical yield of the process, therefore, a double effect is expected, economic and ecologic. Like other advanced agroindustrial residues, the rapeseed straw may be used for the production of biofuel or chemicals by pretreatment and fermentation processes [8,9]. A thermochemical pretreatment step prior to enzymatic hydrolysis is necessary to

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facilitate the access of enzymes to the cellulose and to enhance the rate of hydrolysis by 3–10-fold [10]. The recalcitrance of biomass to enzymatic degradation is believed to be due to the crystallinity of cellulose, to physical barriers formed by lignin and hemicellulose, and to steric hindrances that limit the access of proteins to the cellulose microfibrils [11,12]. The various pretreatment approaches have the common aim of removing or partially rearranging the lignin and hemicellulose, which results in increased enzyme accessibility to the recalcitrant cellulose core, and partial or full decrystallization of the cellulose. The enzyme used to catalyze the hydrolysis of cellulose is cellulase; however, since cellulase cannot degrade hemicellulose and/or lignin, adsorption of cellulase onto the hemicellulose and lignin brings about losses of enzyme effectiveness.

To improve the hydrolysis of cellulose for bioethanol production using an enzyme, the contents of hemicellulose and lignin in the biomass should be reduced through a fractionation processes [13–15]. Current pretreatment technologies can be separated on the basis of their mode of action. Such classification includes mechanical, solvent-based, acid-based, and alkali-based systems. Each vary in their mode of action and in the compounds they produce and, therefore, in the impact they exert on downstream processes [10]. There are several methods that remove hemicellulose from biomass, including methods that fractionate the biomass using acid catalysts at high temperatures. This acid hydrolysis of hemicellulose is a well-established fractionation process for lignocellulosic biomass. Dilute acid pretreatment functions by hydrolyzing the hemicellulose component of biomass into soluble mono- and oligosaccharides consisting primarily of xylose and glucose with comparatively minute quantities of other sugars [16–20]. To remove lignin from lignocellulosic biomass, there are methods that pretreat biomass using alkali catalysts such as sodium hydroxide, aqueous ammonia, sodium nitrate, and lime [11,21,22]. Alkaline pretreatments act to solubilize lignin and/or hemicellulose into the liquid phase and subsequently destabilize the structural components. When biomass is fractionated with alkali catalysts, vinylether-type inter-unit linkage and benzylether-type lignin-carbohydrate linkages between lignin are solubilized, and then extracted from biomass. As a result, the enzymatic digestibility is again improved due to increased amount of effective enzyme for cellulose hydrolysis [7,23–32].

In this study, we investigated the technical feasibility of further improving the glucose yield using a two-stage fractionation process followed by enzymatic hydrolysis of the remaining cellulose. In two-stage fractionation, the first stage was carried out to extract lignin portion using an alkali catalyst, sodium hydroxide. In the second stage process, hemicellulose was extracted using an acid catalyst, sulfuric acid. The objectives of this study were to determine the optimal conditions of two-stage consecutive fractionation process for maximum digestibility from rapeseed straw, to reduce enzyme loading, and to compare with cellulose digestibility from single stage acid pretreatment.

2. Materials and methods

2.1. Feedstock preparation

Rapeseed straw, an agricultural residue, used in this study was provided by Bioenergy Crop Research Center of the National Institute of Crop Science, Rural Department of Administration (Muan, Jeollanam-Do, Korea). It was cut into of 14–45 mesh (0.35–1.41 mm) pieces using a blade mill, followed by drying at 45 ± 5 °C for 24 h before use. The moisture content of raw rapeseed straw after cutting and drying accounted for 5.4% of the total dry weight.

2.2. Carbohydrate analysis

The composition of raw rapeseed straw, the first-stage alkaline fractionation products and the second-stage acid fractionation products were analyzed quantitatively according to NREL laboratory analytical procedures: NREL/TP-510-42618 for Structural carbohydrates, TP-510-42623 for sugars in the liquids or in the hydrolysates [33,34]. The resulting concentrations of dissolved mono-sugar were determined using HPLC (high performance liquid chromatography). A HPLC (Breeze HPLC system, Waters Co., Milford, MA, USA) was used to analyze the components of the samples. Refractive index (RI) detector (Waters 2414, Waters Co., Milford, MA, USA) was used as a detector. Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) and cation H micro-guard cartridge (30 mm × 4.6 mm) (Bio-Rad Laboratories Inc., Hercules, CA) were used as columns. 5 mM H_2SO_4 was used as a mobile phase. The flow rate and the temperature of the column and detector were set as 0.5 mL/min, 60 °C, and 50 °C, respectively. The conversion factor for dehydration on polymerization to glucan was 162/180 for glucose, to XMG (Xylan + Mannan + Galactan) was 132/150 for xylose, mannose, and galactose (xmg), and to arabinan was 132/150 for arabinose. The conversion factor for XMG ignores the factor for mannose and galactose, because xylose is the dominant building unit of the hemicelluloses of most woods and annual plants. Here, XMG (capitalized) represents the sum total of the oligomeric sugar (xylan + mannan + galactan) and xmg (lowercase) represents monomeric sugar.

2.3. The first-stage alkaline fractionation using sodium hydroxide

A study on the removal of lignin through alkaline fractionation was conducted to improve the enzymatic hydrolysis efficiency of raw rapeseed straw. The fractionation experiments were performed using sealed bomb tubular reactors. Twenty centimeter long, 1.07 cm inside diameter with 0.2 cm thickness, and constructed out of stainless steel tubing, capped at either end with Swagelok fittings, giving an internal volume of 17.9 cm^3. The reactor was loaded with 1 g of oven dried rapeseed straw which gave a final ratio of 10 mL of alkaline liquor per g of oven dried rapeseed straw. In order to determine the fractionation conditions for the removal of lignin from the rapeseed straw, reaction temperature, catalyst concentration, and reaction time were set as independent variables, using 0.5–2.0% sodium hydroxide solutions at 130–150 °C and the reaction time of 10–25 min. The lignin removal in fractionated rapeseed straw was evaluated based on percent changes of glucan and xylan compositions according to NREL Laboratory Analytical Procedures [24,25].

2.4. The second-stage acid fractionation using sulfuric acid

Acid fractionation was conducted by setting the reaction temperature, acid concentration, and reaction time suitable for acid fractionation as independent variables to remove hemicellulose from fractionated rapeseed straw. The fractionated rapeseed straw was obtained after the alkaline fractionation was used with drying and not washing. The hemicellulose released into fractionated hydrolyzate, represented by XMG yield, was observed according to changes in reaction conditions. To determine the acid catalyst concentration and reaction temperature, the acid fractionation was conducted using 1.0–4.5% sulfuric acid at 140–160 °C for 5 min. In order to determine optimal reaction time, the acid fractionation was conducted using 3.0% sulfuric acid at 150 °C for 0–30 min. The second-stage acid fractionation was performed using the same physical procedure as for the first-stage alkaline fractionation.