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Comparative study on two-step concentrated acid hydrolysis for the extraction of sugars from lignocellulosic biomass

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HIGHLIGHTS

- Two-step concentrated acid hydrolysis has been conducted with oak, pine, and EFB.
- Oak, pine, and EFB have been characterized in the compositional and XRD analysis.
- Crystalline structure change in raw biomass has been clearly shown in XRD analysis.
- Optimum condition was selected on the highest sugar recovery in the shortest time.
- Pine has the highest recalcitrance based on the CrI and sugar recovery correlation.

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ABSTRACT

Among all the feasible thermochemical conversion processes, concentrated acid hydrolysis has been applied to break the crystalline structure of cellulose efficiently and scale up for mass production as lignocellulosic biomass fractionation process. Process conditions are optimized by investigating the effect of decrystallization sulfuric acid concentration (65–80 wt%), hydrolysis temperature (80 °C and 100 °C), hydrolysis reaction time (during two hours), and biomass species (oak wood, pine wood, and empty fruit bunch (EFB) of palm oil) toward sugar recovery. At the optimum process condition, 78–96% sugars out of theoretically extractable sugars have been fractionated by concentrated sulfuric acid hydrolysis of the three different biomass species with 87–90 g/L sugar concentration in the hydrolyzate and highest recalcitrance of pine (softwood) was determined by the correlation of crystallinity index and sugar yield considering reaction severity.

1. Introduction

The world's energy consumption has progressively increased with the rapid population growth and economic development as more countries have intensified their industrial activities over the last century. Problems of fossil fuel sources such as depletion of unevenly distributed resources, environmental damage caused by greenhouse gases emission, and price fluctuation of oil and gas have increased the need for renewable energy sources. Among many options of renewable energy sources, lignocellulosic biomass is still considered as the only large-scale sustainable carbon source currently available for the future energy supply. The great potential of lignocellulosic biomass utilization has still strongly encouraged the researches that can be applied into industrially and economically viable processes for conversion of biomass to energy, fuels, and chemicals (Moe et al., 2012).

Lignocellulosic biomass refers to nonstarch, fibrous part of plant biomass that is composed of three major constituents: cellulose, hemicellulose, and lignin (Basu, 2010). It can be classified into four main sources: (1) agricultural residues (corn stalk, corn stover, sugarcane bagasse), (2) forestry residues (wood waste, sawdust, mill scrap), (3) energy-woody crops (willow, poplar, switch grass), and (4) industrial and municipal solid wastes (paper mill sludges, recycled newspaper, wasted paper) (Sathitsuksanoh et al., 2010). Lignocellulosic biomass can be processed into biofuel production without competing with food production. In addition, biofuel production from lignocellulosic biomass will generate lignin as residue that can be upgraded into valuable fuel additives or used for

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power generation. The process is designed to reuse all aqueous streams and to convert all solids into economically profitable and useful products (Farone and Cuzens, 1996). Among the various lignocellulosic biomass, wood is one of the most potentially used materials in acid hydrolysis since wood and its residues are the dominant form of lignocellulosic biomass resources (Basu, 2010).

The conversion of lignocellulosic biomass includes two processes: hydrolysis of cellulose into fermentable sugars and fermentation of the sugars to ethanol (Sun and Cheng, 2002). The hydrolysis reaction for cellulose conversion into sugar is principally the degradation of chemical bonds in cellulose, involving the hydrolytic cleavage of β-1,4-glycosidic bond which is catalyzed by H^+ ions of an acid or by the action of a cellulolytic enzyme. The homogeneous hydrolysis of a glycoside in an acid aqueous medium is understood as a replacement process of its initial OR group by a hydroxyl group regenerating H^+ ion by the addition and heterolytic cleavage of a water molecule (Klemm et al., 1998). The acid hydrolysis of glycosidic bonds follows a first-order rate law. The reaction rate depends on the H_3O^+ ion concentration, the reaction temperature, and the chemical environment of the glycosidic bond and the rate is increased with the increasing acid ion concentration and temperature (Klemm et al., 1998; Saeman, 1945).

The conventional methods for hydrolysis process currently are based on thermochemical route (acid-catalyzed hydrolysis) and biochemical route (enzyme-catalyzed hydrolysis), both of which require pretreatment step to utilize lignocellulosic biomass. Among various methods of hydrolysis, concentrated acid hydrolysis, one of the promising methods based on thermochemical route, has several advantages with respect to the milder operating condition (the lower operating temperature and pressure), the higher conversion rate, and the higher sugar recovery. Compared to dilute acid hydrolysis, the advantages of this process are the higher efficiency of sugar recovery, which can reach over 90% of theoretical yield for both glucose and xylose (Guha et al., 2010; Shahbazi and Zhang, 2010; Taherzadeh and Karimi, 2007), and the milder operating temperature and pressure (Iranmahboob et al., 2002) thus the decreasing sugar yield due to inhibitors formation can be minimized (Moe et al., 2012). In comparison with enzymatic hydrolysis, concentrated acid hydrolysis has the higher reaction rate, which directly implies the shorter reaction time. The major challenge in employing enzymatic hydrolysis is finding the appropriate pretreatment and less costly enzyme preparation methods to increase the lignocellulosic substrates availability (Moe et al., 2012; Sun et al., 2011). Due to highly complex and strong recalcitrance of lignocellulosic biomass, the thermochemical route has been regarded more preferable in order to overcome slow reaction by multiple cellulase enzymes (Selig et al., 2013). The disadvantages of concentrated acid hydrolysis are the higher toxicity and corrosivity that required corrosive-resistant reactors or specialized non-metallic constructions and the indispensable need for acid recovery process to make the process economically feasible (Moe et al., 2012; Sun and Cheng, 2002).

Despite the disadvantages, concentrated acid hydrolysis is still attractive and relevant today as this process was claimed to have a low overall cost for the ethanol production (Groenestijn et al., 2006). Arkenol, Inc., a technology and project development company in the United States, has reported that the concentrated acid hydrolysis process could be made economically viable and ready for commercial implementation. Arkenol-developed technology has used commercially available ion exchange resins to separate remaining acid-sugar solution into its acid and sugar components without diluting the sugar. This process was claimed to be capable of producing a clean stream of mixed sugar (both hexoses and pentoses) for fermentation, because the separated sulfuric acid was recirculated and reconcentrated to the level required by decrystallization and hydrolysis steps; and the small quantity of acid left in the sugar solution was neutralized with lime to make hydrate gypsum, $CaSO_4{\cdot}2H_2O$, an insoluble precipitate which could be separated from the sugar solution and used as an agricultural soil conditioner. The Masada Resource Group has also developed full-scale cellulosics-to-ethanol projects in North America (Taherzadeh and Karimi, 2007). Although concentrated acid hydrolysis was previously regarded as economically not viable process due to the requirement of the large amounts of acid, the development of effective acid recovery technologies and the high flexibility of this process toward different feedstocks have renewed its interest (Janga et al., 2012; Moe et al., 2012).

This study aimed to investigate the effect of decrystallization acid concentration, hydrolysis temperature, and hydrolysis reaction time toward sugar recovery in various biomass species. Crystallinity degree of the raw biomass has also been analyzed to conduct a preliminary study about the effect of its crystalline structure on the digestibility of substrate in the hydrolysis process. Although two-step concentrated acid hydrolysis has been a commercialized technology, its application on various lignocellulosic biomass is still an interesting subject to study as the resulting data can be contributed to the researches in biomass utilization area as a basis for the selection of potential lignocellulosic feedstocks.

2. Methods

2.1. Materials and apparatus

Raw biomass used in this experiment were obtained from oak wood, pine wood, and empty fruit bunch (EFB) of palm oil which represented hardwood, softwood, and non-woody biomass, respectively. All the raw biomass was first ground and sieved to pass 18 mesh (1 mm) screen before being fed to the reactor. Sulfuric acid (H_2SO_4, 96%) was purchased from Daejung Chemicals and Metals, Co., Ltd., South Korea. The initial concentrations of sulfuric acid used in decrystallization process were 65, 70, 75, and 80 wt%. The solid loading (acid to biomass) ratio was averagely 2.0 in dry weight basis.

The reactor was 250 mL round bottom flask with four necks (DURAN® Schott, Germany), and equipped with an overhead stirrer (Techno Lab-system, Poong Lim, South Korea) and a Teflon-coated stirring rod. A condenser was used to prevent the vapor product escaped from the reactor during the process. An electric heater was connected to a heating mantle and equipped with a digital temperature controller (DX7, Han Young, South Korea) and a thermocouple. Quenching water was provided to suspend the reaction in the samples in order to prevent further degradation of the desired products.

2.2. Lignocellulosic feedstocks characterization

Feedstocks characterization conducted in this experiment includes: (1) ultimate and proximate analysis (to analyze the elemental composition), (2) compositional analysis (to determine the lignocellulosic component), and (3) crystallinity index analysis (to determine the crystallinity degree) of the raw biomass. Alpha–cellulose fiber (approximately 99.5%) and lignin alkali model compounds were purchased from Sigma Chemical Company and Sigma–Aldrich, USA to determine the crystallinity degree of cellulose used as a comparable reference to the crystallinity degree of raw biomass.

2.2.1. Ultimate and proximate analysis

The ultimate (elemental) analysis was conducted by Advanced Analysis Center at KIST, South Korea. It was carried out in Flash 2000 Organic Elemental Analyzer for carbon (C), hydrogen (H),