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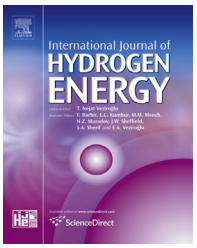

# Effect of severity on dilute acid pretreatment of lignocellulosic biomass and the following hydrogen fermentation

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ABSTRACT

This study aimed to investigate the relationship of the severity of dilute acid pretreatment and the following dark hydrogen fermentation performance. Empty palm fruit bunch, rice husk, and pine tree wood were hydrolyzed in 5% (v/v) $H_2SO_4$ at 10% (w/v) solid/liquid ratio and 121 °C for 30, 60, and 90 min, and then used as the substrate of batch hydrogen fermentation. The maximum sugar yield was achieved at pretreatment with 60 min reaction time; however, it did not guarantee the maximum $H_2$ production. Hydrolyzate obtained from pretreatment where the combined severity factor was at or over 2.01 showed severe 5-hydroxymethylfurfural production and consequent decrease of $H_2$ production rate. Peak $H_2$ production rates of 2640, 3340, and 2565 mL $H_2$ $L^{-1}$ $day^{-1}$ were achieved at the following severity factors: 1.95, 1.86, and 1.83, for empty palm fruit bunch, rice husk, and pine tree wood, respectively.



## Introduction

There is currently a high level of scientific research interest in non-conventional renewable energy sources, which include sugars, starches, and agricultural crops, due to the depletion of fossil fuel and the regulation on greenhouse gas generation. Lignocellulosic biomass derived from energy crops and agricultural residues is a promising alternative renewable source for the promising renewable source for the production of bio-based fuels, which include bioethanol, biodiesel, biogas, and biohydrogen.

While many previous studies have been performed on the use of lignocellulosic biomass for the production of bioethanol, this cannot be said about biohydrogen [1]. Lin et al. [2] reported that the worldwide hydrogen production in 2012 is mainly from natural gas, crude oil, coal, and water analysis. The use of lignocellulosic biomass for biohydrogen production

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has yet to improve production rate and yield to achieve commercial scale to significantly contribute to global biohydrogen production.

Hydrogen-production processes include, but are not limited to, biophotolysis, photofermentation, and dark fermentation. Among these processes, anaerobic dark fermentation provides the most advantages due to its simplicity, lower energy requirements, higher $H_2$ production rates and utilization of waste as raw materials [3]. Monomeric sugars are utilized by fermentative microorganisms during dark fermentation, generally with butyrate and acetate pathways.

Most of the fermentable sugar in lignocellulosic biomass is glucose and xylose in the form of cellulose and hemicellulose polymers, respectively. However, the plant cell wall is a heterogeneous mix of polymers that interact together forming a complex and recalcitrant matrix, making the carbohydrates not easily usable for other processes. The quality and rigidness of the cell wall plays a part in biomass conversion. The relative abundances of the different polymers comprising the lignin part, polymer substitutions, and interactions and modifications among the polymers determine whether the carbohydrates in the lignocellulosic biomass can easily be recovered for other use. One way to modify the structure and interactions of the polymers in the lignin is to perform a physicochemical pretreatment. During pretreatment, polysaccharide-lignin complex interactions are broken, releasing simple, fermentable sugars which are easily utilized by fermentative microorganisms.

Among the various pretreatment methods, dilute acid pretreatment is one of the most widely performed for lignocellulosic biomass. This pretreatment method makes use of harsh physicochemical conditions to recover monomeric sugars from the biomass. The operating conditions, which include reaction time, temperature, acid concentration, and solid/liquid (S/L) ratio of the biomass and acid solution, would affect the efficiency of dilute acid pretreatment significantly [4]. Hsu et al. [5] reported that among dilute acid concentration, reaction temperature, and reaction time, variation of the reaction time showed the highest sensitivity on sugar recovery.

Due to the immense complexity of the lignocellulosic matrix, it is highly improbable that dilute acid pretreatment will be able to break all polysaccharide-lignin linkages, thus it is expected that not all monomeric sugars can be recovered. Therefore, the operating conditions of dilute acid pretreatment should be optimized to obtain maximum monomeric sugar recovery yield. Dilute acid hydrolysis strength can be evaluated using the combined severity factor (CSF), which takes reaction time, temperature, and pH of a particular pretreatment condition [6]. Higher combined severity factors indicate harsher conditions. Harsh physicochemical conditions of dilute acid pretreatment, however, are able to degrade monomeric sugars further into other byproducts, such as 5-hydroxymethylfurfural (5-HMF), furfural, levulinic acid, and formic acid, which are potential inhibitors for fermentative organisms [7]. These inhibitors provide stressful environments for fermentative organisms, resulting to less sugar utilization and lower fermentation productivity. All microorganisms have varying thresholds of maximum concentrations of inhibitors which it is able to withstand [8]. It is also possible that the presence of more than one inhibitor may result to more adverse effects for the microorganisms.

In this paper, dilute acid pretreatment severity was evaluated by not only sugar yield but also the performance of the following dark hydrogen fermentation performance. Three types of lignocellulosic biomass, empty palm fruit bunch, rice husk, and pine tree wood, were pretreated, where the severity was manipulated by changing reaction time. The hydrolyzate was diluted to 10 g $L^{-1}$ total sugar, and then used for the following batch $H_2$ production as the sole substrate.

## Materials and methods

### *Lignocellulosic biomass*

The lignocellulosic biomass samples used in this study were empty palm fruit bunch, rice husk, and pine tree wood pellets. The biomass samples were obtained from local agricultural sources in South Korea. The NREL laboratory analytical procedure [9] was performed to measure the cellulose, hemicellulose, and lignin content in the biomass samples. The carbohydrate, lignin, ash, and extractives content of the samples in dry basis are presented in Table 1.

### *Dilute acid pretreatment*

The lignocellulosic biomass samples were mechanically pulverized until particle size was reduced below 2 mm. The milled biomass was pretreated in 5% (v/v) $H_2SO_4$ (Duksan Pure Chemicals, Korea) at 10% (w/v) S/L ratio in a tightly capped bottle placed in an autoclave (Hanbaek Scientific, South Korea) at 121 °C for 30, 60, and 90 min.

Dilute acid pretreatment resulted to a suspension of solid biomass in hydrolyzate. The liquid and solid components of the hydrolyzate were fractionated via vacuum filtration with 55 mm glass-fiber filters (Whatman, MO, USA). The pH of the liquid portion was then adjusted to 5.5 to 6 using 11–12 mL 8 N NaOH solution.

### *Batch hydrogen fermentation*

Anaerobic digester sludge was obtained from Gyeongsan wastewater treatment plant in South Korea. The pH, alkalinity, total suspended solids (TSS), and volatile suspended solids (VSS) concentration of the sludge were measured to be 7.7, 3.34 g $CaCO_3$ $L^{-1}$, 21.3 g $L^{-1}$, and 16.1 g $L^{-1}$, respectively. The sludge was heated at 90 °C for 30 min to ensure the absence of methanogenic microorganisms and harvest only anaerobic spore-forming $H_2$-producing bacteria [10]. The heat-treated sludge was then used as the inoculum of the following batch $H_2$ fermentation.

The sugar concentration of the hydrolyzate was firstly quantified and an equivalent volume of the hydrolyzate was added to 100 mL serum bottles to obtain 30 mL hydrolyzate solution with initial sugar concentration of 10 g $L^{-1}$. This initial sugar concentration was previously found by the authors [11] to provide the highest hydrogen production using hydrolyzate of lignocellulosic biomass. 5 mL inorganic

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