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Generation of electricity from $FeCl_3$ pretreatment of rice straw using a fuel cell system

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HIGHLIGHTS

- ▶ We observed that a great deal of ferric iron was reduced to ferrous iron during $FeCl_3$ pretreatment of rice straw.
- ▶ $FeCl_3$ acts not only as an oxidant to oxidize both xylose and lignin but also as a catalyst to hydrolyze hemicellulose.
- ▶ Ferrous iron could be completely removed from liquid hydrolysate while generating electricity using a fuel cell system.
- ▶ The optimal conditions for the fuel cell performance were a pH of 7.0 and ferrous iron concentration of above 0.008 M.

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ABSTRACT

This study explored a new approach to the pretreatment of lignocellulosic biomass using $FeCl_3$ combined with a fuel cell system to generate electricity. After pretreatment, ferric iron (Fe^{3+}), a strong catalyst in the hydrolysis of carbohydrate, was found to be reduced to ferrous iron (Fe^{2+}) by means of the oxidation of xylose and lignin. Ferrous iron, as a fuel, was employed to the anode part of a fuel cell, generating power of 1110 mW/m^2. During the fuel cell operation, ferrous iron was completely removed through oxidation to ferric iron and precipitated out. The optimal conditions for the operation of the fuel cell were found to be a pH of 7.0 and ferrous iron concentration of above 0.008 M. These results clearly show that a fuel cell system could be used not only to remove ferrous iron from liquid hydrolysate, but also to produce electricity.

1. Introduction

Increasing concerns about climate change and energy crisis have driven rather aggressive research activities to seek alternatives to fossil fuel. Lignocellulosic biomass obtained from agricultural residues, wood, and energy crops is considered as a promising renewable substitute (Lin and Tanaka, 2006); the production of biofuels, including bioethanol, is cheap and does not compete with food crops (Alvira et al., 2010). However, lignocellulose-based bioethanol is not yet commercially viable due to its currently unsolved economic and technical obstacles (Sánchez and Cardona, 2008). Its cost-effective production certainly requires a multi-faceted approach, synergistically using microbiological, physical, chemical, and even electrochemical processes.

Lignocellulose, the most abundant organic matter on earth, is mainly made up of cellulose, hemicellulose, and lignin. Its natural complex structure makes it recalcitrant to enzymatic and microbial attacks (Ding and Himmel, 2006; Zhang and Lynd, 2004). To make this persistent biomaterial more susceptible to sequential enzymatic hydrolysis, therefore, pretreatment is absolutely required. The pretreatment, whose primary goal is to disrupt the complex and crystalline structure of cellulose, however, is highly energy-intensive and thus its efficiency needs to be dramatically improved for the commercialization of its final products such as bioethanol (Mosier et al., 2005).

In this study, we attempted to lower the cost of overall pretreatment via combining a fuel cell system that generates electricity with a pretreatment process using $FeCl_3$. It has been reported that pretreatment with $FeCl_3$ could remove linkages between lignin and carbohydrates (Liu et al., 2009; Kim et al., 2010). Ferric iron (Fe^{3+}) is a strong catalyst on the oxidation process and has a far stronger catalytic effect on hemicellulose than cellulose (Yan et al., 1996). It was observed that a great deal of ferric iron was reduced to ferrous iron (Fe^{2+}) during $FeCl_3$ pretreatment of rice straw. To this end, we employed a ferrous-based fuel cell system in this study: ferrous iron, found in liquid hydrolysate after $FeCl_3$ pretreatment, was fed to the anode of the fuel cell system where it is oxidized to ferric iron as a fuel. Several studies have reported the ferrous-based fuel cell system for the sole purpose of generating

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electricity (Cheng et al., 2007; Eom et al., 2011). It was demonstrated that ferrous iron could be completely removed from liquid hydrolysate while generating electricity using the fuel cell system. To find the optimal conditions for producing the maximum power, the pH and iron concentration of the anode part were investigated.

2. Methods

2.1. Lignocellulose

The rice straw used in this experiment was harvested from Nonsan field near Daejeon in Korea. The rice straw was milled and screened to achieve a size of less than 50 mesh prior to pretreatment, and air-dried at 45 °C. The composition of the rice straw was analyzed according to NREL-LAP and was 36.5% glucan, 20.8% xylan, and 16.9% lignin on dry weight basis (Sluiter et al., 2008).

2.2. $FeCl_3$ pretreatment

Pretreatment was conducted in a stainless steel reactor (∅26 mm × 132 mm with 70 mL of volume) coated with Teflon on the inside. For the pretreatment, 5 g of rice straw and 50 mL of 0.1 mol/L $FeCl_3$ solution at 10% (w/v) solid loading were mixed together in the reactor for 1 h before heating. Then the reactor was heated to the desired temperatures. When a reaction ended, the reactor was cooled down to room temperature. At the end of the pretreatment, solid residue was collected by filtration for subsequent enzymatic hydrolysis and liquid fraction was separated for application to a fuel cell system. The flow chart for integrated system combining $FeCl_3$ pretreatment and ferrous fuel cell is shown in Fig. 1.

2.3. Enzymatic hydrolysis

The enzymatic hydrolysis of the pretreated substrate was carried out in 50 mM sodium citrate buffer (pH 4.80) containing 40 μg/mL tetracycline and 30 μg/mL cycloheximide according to the National Renewable Energy Laboratory (NREL) standard procedures (Selig et al., 2008). A mixture of cellulase from *Trichoderma reesei* (Celluclast 1.5L, Sigma) with an activity loading of 60 FPU/g cellulose and β-glucosidase from *Aspergillus niger* (Novozyme 188, Sigma) with an activity loading of 30 CBU/g cellulose was used for the enzymatic hydrolysis (Emmel et al., 2003). The enzymatic hydrolysis reaction mixture was incubated at 50 °C and 170 rpm for 72 h in a shaking incubator and the hydrolysates were sampled periodically for sugar analysis.

2.4. Analysis of rice straw

The composition of the untreated and pretreated rice straw was determined according to Laboratory Analytical Procedures from NREL (Sluiter et al., 2008). At first, a sample was treated with 72% H_2SO_4 at 30 °C for 2 h in a shaking water bath. The reaction mixture was then diluted to 4% H_2SO_4 and autoclaved at 121 °C for 1 h. The sugar contents in the samples were determined by a HPLC system equipped with a reflective index detector (Agilent 1200 series, USA) and an Aminex HPX-87P column (Bio-Rad, USA). The mobile phase in the column was water at a flow rate of 0.6 mL/min. The remaining solid residue was dried overnight at 105 °C and further placed in a muffle furnace at 575 °C for 24 h a lignin analysis.

2.5. Ferrous-based fuel cell

The fuel cell reactor consisted of two Plexiglas chambers, each with a respective volume of 100 mL (Fig. 2). The anode and cathode parts were separated from each other by an anion exchange membrane (AHA, Astom, Japan). All electrodes were made of carbon cloth (type A, E-TEK) with a projected surface area of 15 cm^2. The cathode electrode was loaded by platinum (10 wt.% Pt/C, Alfa Aesar, 0.5 mg/cm^2). The hydrolysate from the $FeCl_3$ pretreatment, after being diluted, was introduced to the anode compartment and dissolved air was employed as a terminal electron acceptor in the cathode chamber. In a preliminary test to find the optimal conditions of pH and ferrous iron concentration, $FeCl_2$ was used in the anode chamber as a fuel. The initial pH of the electrolytes was maintained using McIlvaine's buffer solution (0.2 M Na_2HPO_4 and 0.1 M citric acid).

Cell voltage across an external resistor of 1 kΩ in the circuit of the fuel cell system was recorded at 10 min intervals using a multimeter (Keithley 2700). Maximum power density was measured from linear sweep voltammetry (LSV) utilizing a potentiostat (CHI 604C) and it was normalized to the projected surface area of the anode. Ferrous iron and total iron concentrations were measured by UV–Vis spectrophotometer (DR 5000, HACH).

3. Results and discussion

3.1. $FeCl_3$ pretreatment

The solid compositions of untreated and pretreated samples with $FeCl_3$ are listed in Table 1. Most of the hemicellulose was degraded with about 80% of glucan remained when rice straw was

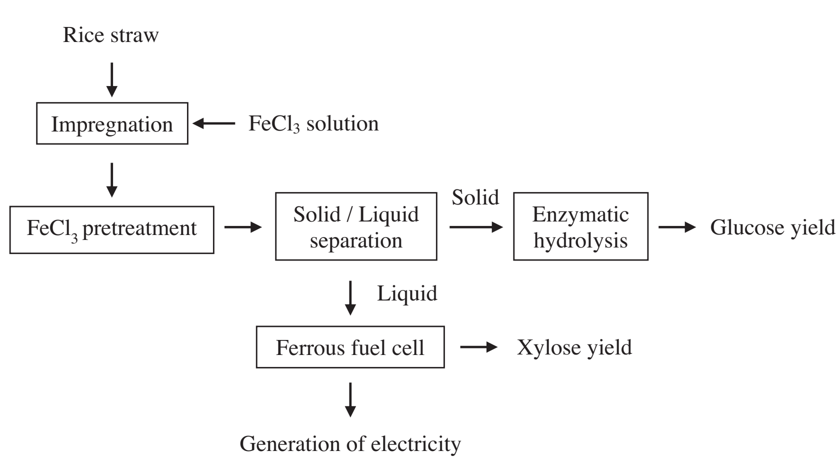

Fig. 1. The flow chart of the proposed integrated process of $FeCl_3$ pretreatment and ferrous fuel cell.