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Enhancing enzymatic hydrolysis and biogas production from rice straw by pretreatment with organic acids

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ABSTRACT

Lignocellulosic biomass is recalcitrant to enzymatic and microbial degradation due to its chemical compositions and physical structures that inhibit the hydrolysis reactions. To obtain a high sugar yield for biofuel production, pretreatment process is generally needed to improve efficiency of hydrolysis. Here, organic acids were used to pretreat rice straw. Using Response Surface Methodology (RSM), the effect of three pretreatment parameters, including acid concentration, treatment time, and reaction temperature, on pretreatment efficiency were evaluated and used to generate mathematic optimization model. The hydrolysis results indicated that oxalic acid pretreatment led to the highest enhancement of enzymatic saccharification up to 213.4 mg (starting from 500 mg of pretreated sample) when using 5.01% oxalic acid concentration at 135.91 °C for 30.86 min, which was 2.68 times higher than the untreated rice straw. The structural changes in the pretreated biomass were investigated using FT-IR analysis. The results suggested that lignin composition was significantly removed from the pretreated biomass, and the crystalline cellulose was also modified to amorphous form during pretreatment. Both untreated and pretreated rice straw were subjected to anaerobic digestion to evaluate the influence of organic acid pretreatment on biogas production. The highest biogas yield was 322.1 ml/g-rice straw when using citric acid pretreatment which was 7.40 times higher than untreated biomass. These results demonstrated that organic acids can be used for pretreatment of lignocellulosic materials to enhance hydrolysis and biogas production.

1. Introduction

Methane emissions from deep water rice cultivation significantly contribute to the greenhouse gas emissions worldwide (Ali et al., 2013; Vibol and Towprayoon, 2010; Zhang et al., 2014). The uncontrolled gas emissions result from anaerobic digestion of biomass during the flooding period of the cultivation. The biomass, mainly rice straw, left on the fields throughout the fallow period and is burnt before land preparation for next cultivating seasons. Reduction of these rice straws with good practices will reduce methane emissions to environment (Ahn et al., 2014; Knox et al., 2015). Indeed, the development of the controlled fermentation of rice straw to produce biofuels, such as in an anaerobic digester for biogas production, can achieve this end of fewer emissions.

Rice straws are lignocellulosic materials consisting of three types of major components, including cellulose, hemicellulose, and lignin. Both cellulose and hemicellulose could be hydrolyzed to monosaccharides or simple sugars that, subsequently, could be fermented to biofuel (Blanch et al., 2011). However, one of most important problem to produce biofuel from lignocelluloses is the resistance of biomass to biodegradation or hydrolysis (Agbor et al., 2011; Chandel and Singh, 2011). The key success factor for biofuel production is to increase the efficiency of biomass hydrolysis by enhancing the enzyme accessibility via pretreatment method. During this decade, there are growing in numbers of intensive studies to develop pretreatment methods (Chandel and Singh, 2011; da Costa et al., 2009; Hendriks and Zeeman, 2009). However, there are still a number of technological, market and policy barriers that are

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serious obstacles to the economic feasibility and competitiveness of such process.

Previously, inorganic acid pretreatment such as sulfuric acid (Baadhe et al., 2014; Sindhu et al., 2011), hydrochloric acid (Sindhu et al., 2011), and nitric acid (Kim et al., 2014) has been widely studied due to their high efficiency, and relatively low cost, however using these strong acids can cause highly corrosion to the equipments, and undesired environmental problems. Organic acids, such as acetic acid (Zhao et al., 2014), oxalic (Lee et al., 2010; Scordia et al., 2011), maleic (Lu and Mosier, 2007), and fumaric acid (Kootstra et al., 2009a), were investigated as alternative options, despite their concentrations used for pretreatment are relatively high compared to inorganic acids. Sometimes, organic acid pretreatment was classified as organosolv pretreatment and has been employed for pulping of wood and herbaceous plants (Zhao et al., 2009). Dilute organic acid pretreatment has some desirable characteristics, including effective hydrolysis, less degradation products and more xylan sugars (Kootstra et al., 2009b; Qin et al., 2012). Nevertheless, organic acid pretreatment is still received less attention and so far relatively little is known about the its mechanism on pretreatment.

In this study, three organic acid pretreatments were carried out to pretreat rice straw. The pretreatment conditions were optimized to maximize released sugar contents. The influence of pretreatment parameters were determined experimentally on a laboratory scale based on the Response Surface Methodology (RSM). The structural and chemical changes of the pretreated rice straw were also monitored. Each pretreated sample was used as substrates in anaerobic fermentation and the effect of these organic acids pretreatment on biogas production from rice straw were investigated.

2. Materials and methods

2.1. Preparation and analysis of rice straw

Rice straw was obtained from a local rice field in Ayuthdhaya province, Thailand. The biomass was dried in hot air oven at 80 °C until constant weight was achieved, then it was ground and screened to a 10–20 mesh size. Five grams of dried rice straw were used for each pretreatment reaction. The ground biomass was kept in sealed plastic bag until used in pretreatment. Contents of cellulose, hemicelluloses and lignin of rice straw were determined using the method described by Van Soest and Wine (1967) (Van Soest and Wine, 1967). The total solids (TS) and volatile solids (VS) were tested according to the standard water and wastewater examination methods (APHA, 2005). The contents of cellulose, hemicellulose, and lignin in rice straw were 34.63%, 29.74%, and 15.34% respectively. The total solids (TS) and the volatile solids (VS) content of rice straw were 90.73% and 85.66%, respectively.

2.2. Organic acid pretreatment of rice straw

Design-Expert software (version 7.0.0 Stat-Ease, USA) was used to generate the RSM experimental design, to statistically analyze experimental data, to construct mathematic model, and to calculate optimized condition. Box-Behnken Design was applied in this study with a total of 17 runs (Box and Wilson, 1951; Sriariyanun, 2014). The tested parameters of pretreatments (independent variables) were reaction time (X_1), pretreatment temperature (X_2), and acid concentration (X_3). The dependent variable was sugar yield (Y). These three tested factors were selected in this study because they are easily adjusted during operation for further scale-up process. Furthermore, these factors have been demonstrated to significantly affected the pretreatment efficiency in many studies (Kootstra et al., 2009a; Kootstra et al., 2009b; Lee et al., 2010; Lu and Mosier, 2007; Scordia et al., 2011; Zhao et al., 2014). The pretreatment conditions were organic acid concentrations of 5–15% (w/w) or inorganic acid concentrations of 0.5–2% (w/w), temperatures of 100–140 °C, and reaction times of 30–60 min. The coded value levels of the independent variables were designated in corresponding to actual value as shown in Table 1 (including max = +1, mid = 0 and min = −1). The experimental data were analyzed by using statistical software to accommodate the second-order polynomial regression model:

Table 1
Value of independent variable with corresponded coded level.

Factor	X_1	X_2	X_3
Code	−1	0	1
Temp(°C)	100	120	140
Time (min)	30	45	60
Conc. organic acid (%wt)	5	10	15
Conc. Inorganic acid (%wt)	0.5	1.25	2.0

$$Y = \beta_0 + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum_{i=1}^{2}\sum_{j=i+1}^{3}\beta_{ij} X_i X_j$$

In this study, three types of organic acids including acetic acid ($C_2H_4O_2$), citric acid ($C_6H_8O_7$) and oxalic acid ($C_2H_2O_4$) were selected for pretreatment experiments. Hydrochloric acid (HCl), as an inorganic acid, was additionally tested to compare with the organic acids. All pretreatments were performed in a screw-capped bottle with 10% (w/w) of rice straw loading in each acid solutions (total reaction volume of 50 ml). The samples were then heated in a hot air oven with the set parameters of temperature and time based on the RSM experimental design. After pretreatment, solid residue was separated by filtration using fritted-glass filter and washed with deionized water for three times. Samples were dried at 80 °C until constant weight was achieved, and were kept in sealed bags until used in subsequent enzymatic hydrolysis.

2.3. Enzymatic hydrolysis

Pretreatment efficiency of each experimental run was assessed based on degree of saccharification of the pretreated rice straws using cellulase enzyme mixtures containing 20 FPU/g-substrate of Celluclast 1.5 l (Sigma-Aldrich, USA) and 100CBU/g-substrate of Novozyme 188 (Sigma-Aldrich, USA) (Ghose, 1987; Sriariyanun et al., 2015). Each enzymatic hydrolysis experiment was conducted separately in a screw-capped plastic tube (containing 50 mM sodium citrate buffer (pH 4.7) with 20 ml of working volume, 0.5 g of pretreated biomass and 200 μl of 2 M sodium azide). The reactions were incubated at 45 °C for 72 h in a 200 rpm shaking incubator. The amount of liberated reducing sugars of hydrolysate was determined using the 3,5-dinitrosalisylic acid (DNS) method (Miller, 1959).

2.4. Anaerobic fermentation of pretreated rice straw

The influence of each organic acid pretreatment on biogas production was assessed by anaerobic digestion experiment. The seed inoculum, anaerobic wastewater sludge, used for biogas production was obtained from municipal wastewater treatment plant in Bangkok, Thailand. The characteristics of the seed inoculum were pH of 7.3 ± 0.05, 65.8 ± 0.66 g/l of total solid (TS), and 38.6 ± 0.45 g/l of total volatile solid (VS) (APHA, 2005). The COD values of samples were determined based on standard method (APHA, 2005). The inoculum was starved for 48 h prior to the start-up of the assays, by incubating at 35 °C and 100 rpm agitation without substrate. Batch biogas production experiments were performed in sealed Erlenmeyer flasks with 500 ml of working volume containing 3% (TS)