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A rapid and efficient hydrothermal conversion of coconut husk into formic acid and acetic acid

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ABSTRACT

Coconut husk is an abundant cellulose/lignin-rich biomass waste in tropic and subtropical zone. Although the resource utilization of coconut husk has aroused considerable concerns, highly-efficient and selective conversion of coconut husk into chemicals is difficult due to its stable coexistence structure of cellulose and lignin components. Herein, a facile and high selectively conversion of coconut husk into value-added organic acids of formic and acetic under mild hydrothermal conditions was proposed for the first time. It was found that a simple acidic pretreatment is efficient for obtaining high yield of formic and acetic acids. The highest yield of total acids can reach up to 50.2%, which is the reported highest yield of formic acid and acetic acid from ligno-cellulosic biomass. This work exemplifies the possibility of complex coconut husk waste valorization to value-added chemicals, which is not only solve the problems of coconut husk waste pollution, but also provide an alternative route for fuel production from renewable resources.

1. Introduction

Conversion of biomass, the most abundant carbon-neutral and renewable resources on earth, into value-added chemicals and fuels has attracted considerable attention as an important method to reduce greenhouse gas emissions and to alleviate the current dependence on fossil fuels [1,2]. Coconut husk is an abundant cellulose/lignin-rich biomass waste and widely distributed in tropic and subtropical zone [3]. For example, the annual output of coconuts in Hainan province of China has reached more than 200 million, but it accounts for only 0.04% of the world's total output. The cellulose in coconut husk is composed of tiny fibers, which form a reticular skeleton, while hemicellulose and lignin are filled between the micro fibers, which act as 'adhesives' and 'fillers'. Coconut husk is hard to be treated because of this special structure and the disposal of waste coconut husk has become a worldwide problem. Traditional methods of coconut conversion focus on gasification to syngas, and pyrolysis to bio-oil or activated carbon [4–7]. However, these thermal treatments are commonly accompanied with the coking of coconut and noble metals are employed as catalyst [8,9]. In fact, conversion of coconut husk into useful chemicals is more important than direct utilization as energy because inexhaustible energy would be supplied from solar or nuclear energy in the future while chemical production must rely on the carbon-based materials. Therefore, developing a new strategy for conversion of coconut husk into value-added chemicals is necessary.

Owing to the unique properties of high-temperature water, such as a low dielectric constant, a high ion product and an increased diffusivity compared with room temperature water, hydrothermal reactions have demonstrated to be highly efficient in the conversion of biomass and biomass derivatives [10–12]. Hydrothermal treatment is particularly suitable for the valorization of organic wastes in a green way, since environmentally benign water it used as the reaction medium and reaction temperature is comparatively low and nearly cost-free. Moreover, hot-temperature water facilitates the decomposition of cellulose and lignin into useful low molecular weight substances [13,14]. Many researches on the hydrothermal conversion of organic waste into fuels and chemicals have demonstrated that hydrothermal reactions enable rapid conversion of various organic materials into useful chemicals [11,15–17]. However, facile transformation of hardly decomposed biomass/waste such as cellulose/lignin-rich coconut husk, with high selectivity and high yield still remains a significant challenge due to stable coexistence structure of cellulose and lignin components.

As two vital commodity chemicals, formic acid and acetic acid are widely used in pharmaceutical synthesis, leather tanning and dyeing industry. Especially, recent research has demonstrated that formic acid has the potential to serve as an excellent hydrogen storage carrier and as clean fuel cell material since its dehydrogenation can easily proceed under mild conditions over catalyst [18–20]. In previous works, we had

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developed hydrothermal method to convert monosaccharides to formic acid or acetic acid [11,21,22]. A 80% yield of formic acid and 23% yield of acetic acid were achieved from selective conversion of glucose, respectively [21,23,24]. Selective conversion of polysaccharides and lignin is still challenging. Herein, we present a new approach of the hydrothermal conversion of coconut husk into formic and acetic acids with a facile acidic pretreatment.

2. Experimental section

2.1. Materials

Coconut husk, which are obtained from Hainan Province, China, was used as the initial reactants. After drying in the oven, the coconut husk was grinded into 50-mesh powder by a ball mill (QM-3SPO4, planetary ball mill). NaOH (≥96%), H_2O_2 (30%) and HCl (36% ~ 38%) were provided by Shanghai Lingfeng Chemical Reagent Co., Ltd. The oxidant used in the experiment is H_2O_2, assuming 1 mol of H_2O_2 gives 1/2 mol of O_2. Pure cellulose and alkali lignin were purchased from Sigma-Aldrich. Additionally, formic acid, acetic acid, propionic acid, fumaric acid and furfural, which were obtained by Sinopharm Chemical Reagent Co., Ltd, were also used as test materials. All reagents in this study are of analytic-grade and were used without further treatment.

2.2. Experimental procedure

The typical experimental procedure was shown as follows. 0.05 g coconut husk powder as starting material was used in all experiments. A Teflon-lined stainless steel batch reactor with an internal volume of 30 mL was used in acid-pretreated procedure, avoiding the influence of metal ions caused by acid corrosion of reactor wall. First, the Teflon reactor was putted into a preheated oven for acidic pretreatment procedure. After desired reaction time, the reactor was took out and allowed to cool down naturally to room temperature. Then, the pretreated samples were added into a SUS316 batch reactor (internal volume 5.7 mL) for the hydrothermal oxidation procedure. After a shake process to enhance mixing, the reactor was putted into a salt bath for reaction. Finally, the reactor was taken out and cooled with cooling water. The liquid sample was collected and filtered by 0.22 μm Syringe Filter for analysis

2.3. Product analysis

The liquid sample was analyzed by a GC–MS (Agilent 7890A GC system, 5975C inert MSD with Triple-Axis Detector) equipped with an HP-Innowax column (Dimension: 30m × 250 μm × 0.5 μm) and HPLC (Agilent 1260 serials equipped with UV–vis detector) with Shodex RSpak KC-811 column. The mobile phase was 2 mM $HClO_4$ with a flowing rate of 1 mL min^{-1}. The amount of carbon in feedstock input was measured by elemental analyzer and the proportion of carbon was 40%.

The yield of product was calculated as the following equation. The experimental data error is within 5%.

$$Y=\frac{\text{moles of carbon in products}}{\text{moles of carbon in feedstock input}}\times 100$$

3. Results and discussion

3.1. Efficiency of hydrolysis pretreatment for improving the yield of formic acid and acetic acid

Initially, direct oxidized treatment of coconut was performed under similar hydrothermal conditions referred to glucose conversion. Fig. 1 shows a HPLC chromatogram of liquid products obtained after direct

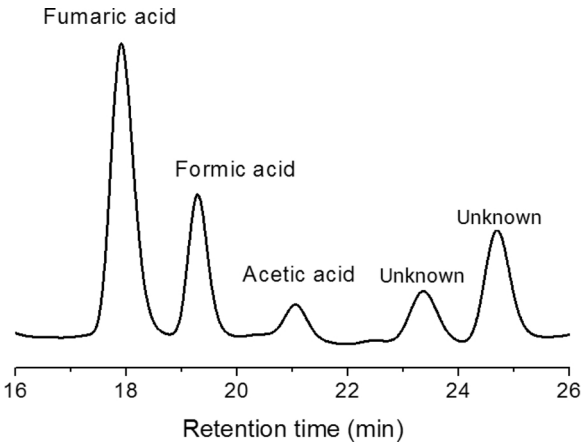

Fig. 1. HPLC chromatogram of products from coconut husk with direct hydrothermal oxidation (250 °C, 1 min, 1 mol/L NaOH, 120% oxygen supply).

hydrothermal oxidation. There are three obvious peaks except unknown substances, fumaric acid, formic acid and acetic acid. Although the peak of fumaric acid is strong due to the sensitivity of UV detector for double bond, the quantitative results show that the yield of fumaric acid is less than 1%. The yields of formic acid and acetic acid are 9.0% and 10.3%, respectively. The reason of low yield of formic acid and acetic acid from coconut husk is probable due to the different decomposition routes of cellulose and lignin from glucose under alkali hydrothermal oxidation conditions. If cellulose and lignin are decomposed to monomers (e.g. glucose) and then proceeds oxidized reaction, the yield of formic acid or acetic acid would be improved. Thus, acidic pretreatment procedure was chosen for improving of the glucose yield in this study. In the acid pretreatment, considering that oxidizing acid such as H_2SO_4 and HNO_3 will lead to oxygenolysis of coconut husk, a non-oxidizing acid HCl was employed, and a moderate concentration of 1.2 mol/L HCl was used because a low concentration of acid affects the rate of cellulose hydrolysis, whereas a higher concentration of acid leads to cellulose carbonization.

Two important components of coconut husk, cellulose and alkali lignin, were initially studied with hydrolysis pretreatment. As shown in Fig. 2a&b, both formic and acetic acids yield increased significantly with hydrolysis. Quantitative analysis showed the yield of formic acid and acetic acid increased from 20.1% and 11.7% to 44.4% and 24.4% for cellulose, and 13.2% and 11.4% to 30.1% and 23.4% for lignin. These results indicate hydrolysis pretreatment is efficient for increasing the yield of organic acids. Therefore, coconut husk was conducted acidic hydrolysis before oxidation procedure. As envisaged, the yields of formic and acetic acids increased from 9.1% and 9.72% to 23.6% and 21.6%, respectively (Fig. 2c). Further, the liquid samples after hydrolysis and oxidation were analyzed by GC–MS (Fig. 3). Acetic acid, furfural and propionic acid were detected after pretreatment. The formic acid was not observed due to the insensitivity of Innowax column to it. Subsequent hydrothermal oxidation procedure proceeded and the peak of furfural nearly disappeared probably because it was converted to acetic acid [12].

3.2. Effects of the reaction parameters on the yields of formic acid and acetic acid

To obtain the optimal reaction conditions for formic and acetic acids production, effects of reaction time of pretreatment, alkali concentration, oxidant amount, reaction time and temperature in oxidation procedure were investigated.

First, the influence of pretreatment time on the conversion of coconut husk was investigated. As displayed in Fig. 4, the yield of formic acid and acetic acid increased obviously from 11.5% and 3.3% to 23.0%