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Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment

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ABSTRACT

Pretreatment of lignocellulosic biomass is of the utmost importance for the development of bioethanol because of the abundance and low cost of lignocelluloses. To figure out the hydrolysis characteristics of sugarcane bagasse in a microwave irradiation environment, the biomass is pretreated by a dilute sulfuric acid solution at 180 °C for 30 min, with the concentration ranging from 0 to 0.02 M. A variety of analyses, including fiber analysis, TGA, XRD, FTIR and HPLC, are employed to aid in understanding the physical and chemical characteristics of residual solid particles and solutions. A higher concentration is conducive to destroying bagasse; however, the buffering capacity possessed by the biomass is also observed in the pretreatment. The experimental results indicate that around 40–44 wt% of bagasse is degraded from the pretreatment in which around 80–98% of hemicellulose is hydrolyzed. In contrast, crystalline cellulose and lignin are hardly affected by the pretreatment. The maximum yields of xylose and glucose as well as the minimum furfural selectivity occur at the acid concentration of 0.005 M. Consequently, the aforementioned concentration is recommended for bagasse pretreatment and bioethanol production.

1. Introduction

Bioethanol is an important fuel nowadays because it has been widely blended with oil and consumed in internal combustion engines for the power of vehicles [1–4]. Currently, most of the bioethanol is produced from maize or sugarcane [5]. When bioethanol is produced from the aforementioned feedstocks, the raw materials account for around 40–70% of the production cost [6]. For the mass production of bioethanol, it is always desirable to use cheaper and more abundant substrates. Lignocelluloses, which can be obtained from the wastes of forest industry, energy crops, agricultural residues and grass, have been considered as attractive feedstocks for the prospective production of bioethanol, because of its low cost, availability in large quantities and low risk of causing food storage [7,8].

Lignocelluloses consist mainly of hemicelluloses, cellulose and lignin [9,10]. Hemicelluloses are branched polysaccharides containing sugar residues, such as xylose, mannose, galactose, glucose, arabinose and glucuronic acid [11]. Cellulose is a linear polymer of glucose in which crystalline and amorphous structures are contained [12]; lignin is an amorphous polymer made up of aromatic derivatives [13]. In order to produce bioethanol from lignocelluloses, it is essential to obtain fermentable sugar from hemicellulose and cellulose, especially for the latter. However, by virtue of lignocelluloses featured by recalcitrance in nature, the process of biomass pretreatment is required [14]. The purposes of pretreatment are to remove hemicellulose and lignin, decrease crystalline cellulose and increase the surface area of the materials [15], thereby facilitating the subsequent enzymatic hydrolysis. As a matter of fact, studies have suggested that pretreatment is the most important step for bioethanol production from lignocelluloses in that it defines the extent to and cost at which the carbohydrates of hemicellulose and cellulose can be converted to bioethanol [16].

As far as biomass pretreatment is concerned, a number of methods, such as mechanical pretreatment, alkali or acid pretreatment, steam explosion, ammonia fiber explosion, hot water, supercritical CO_2 treatment, ozone pretreatment and biological pretreatment, have been developed [16]. Alkaline pretreatment has received a lot of attention lately because it can remove lignin from biomass, thus improving the reactivity of the remaining polysaccharides and removing acetyl groups and various uronic acid substitutions on hemicellulose. In the study of Fuentes et al. [17] upon sugarcane bagasse pretreatment with lime, they found that the maximum glucose yield was 228.45 mg (g raw biomass)$^{-1}$, corresponding to 409.9 mg (g raw biomass of total reducing sugars)$^{-1}$, with the pretreatment performed at 90 °C, for 90 h, and with a lime loading of 0.4 g (g dry biomass)$^{-1}$. Rodrigues et al. [18] focused on the potential of microwave-assisted alkali pretreatment to improve the rupture of the recalcitrant structures of the cashew able bagasse. With the alkali concentration of 0.2 and 1.0 mol L^{-1}, solid percentage of

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16% (w/v) and enzyme load of 30 FPU g_{CAB-M}^{-1}, pretreatment time and microwave power had no significant effect on glucose concentration. Despite the advantages of alkali pretreatment utilizing lower temperatures and pressures compared to other pretreatment technologies, the pretreatment time is measured in terms of hours or days rather than minutes or seconds.

Among the developed methods, the pretreatment using dilute sulfuric acid has been thought of as one of the most cost-effective methods [19,20]. To achieve a dilute acid pretreatment, the mixture of biomass and dilute acid solution is usually controlled at a moderate temperature by means of conventional heating [21–23]. In conventional conduction and convection heating, thermal energy is delivered through superficial heat transfer. In addition to conventional heating, microwave-assisted heating is another effective route to pretreat biomass. In microwave-heating processes, materials containing dielectrics are heated by converting microwave irradiation through molecular interactions in electromagnetic fields [24], that is, the electromagnetic energy is converted into thermal energy through dielectric heating. Moreover, the electromagnetic field used in microwaves may create non-thermal effects that also accelerate the destruction of crystal structures [25].

In the study of Palmarola-Adrados et al. [26], they pretreated starch-free wheat fibers in dilute sulfuric acid solutions using microwave heating; it was illustrated that the biomass pretreatment with microwave heating was able to give a higher sugar yield compared to steam explosion. Hu et al. [27] used a radio-frequency-assisted (RF-assisted) heating method to pretreat switchgrass in a NaOH solution. They mentioned that the RF-assisted heating resulted in a higher xylose yield than the conventional heating. In addition, the enzymatic hydrolysis of RF-treated solids led to a higher glucose yield than the corresponding value obtained from the conventional heating. Li et al. [28] carried out the pretreatment of swine manure in sulfuric acid solutions heated by microwaves; it was outlined that microwave irradiation could lead to a higher yield of reducing sugar, shorter reaction time and lower energy consumption so that it was a suitable technique for the saccharification process of swine manure. Zhao et al. [29] used a NaOH solution to pretreat rice hulls in a microwave environment; they mentioned that the increased accessibility of the substrates by microwave pretreatment was mainly achieved by the rupture of the rigid structure of rice hulls, and the reducing sugar content was increased by 13% compared with that of rice hulls without pretreatment. In the study of Nikolić et al. [30], microwaves and ultrasound were individually employed to pretreat corn meal. It was reported that the application of microwave pretreatment resulted in higher yields of glucose and bioethanol when compared to the ultrasound pretreatment. They also pointed out that the application of microwave pretreatment could decrease the time of simultaneous saccharification and fermentation, thereby effectively reducing the production cost of bioethanol. In the study of Lu et al. [31], they also pointed out that, unlike conventional heating, microwaves generate higher power densities, enabling higher production rates and lower production costs.

From the foregoing literature, it is evident that microwave heating is an effective and promising method to pretreat biomass for bioethanol production. To understand the impact of microwaves on the disruption of biomass structure, bagasse pretreated via microwave-assisted heating in a dilute sulfuric acid solution (0.2 M) has been preliminarily performed in a previous study [32]. It was found that an increase in reaction temperature intensified the destruction of the lignocellulosic structure of bagasse in a significant way and the pretreated bagasse particles were simultaneously characterized by fragmentation and swelling. Unfortunately, the influence of dilute acid concentration on the disruption of biomass structure and the analysis of the liquid phase were absent. It is known that dilute acid pretreatment is able to convert hemicellulose contained in lignocellulosic biomass to soluble sugars and facilitates the subsequent enzymatic hydrolysis of cellulose [16,20,33]. However, the hydrolysis of polysaccharides also leads to the formation of sugar degradation products, namely, inhibitors, such as furfural and 5-hydroxymethylfurfural (HMF) [21]. Degradation products not only reduce the yields of sugar monomers but also act as fermentation inhibitors. To produce fermentable hydrolysates and prevent a high loss in sugar yields, it is therefore necessary to choose reaction conditions that keep the generation of inhibitors at a lower level. To date, many efforts are being done to improve processes and develop new technologies so as to achieve further conversion of available sugars from sugarcane bagasse. However, the work is currently being done at laboratory and pilot plant scales and practical applications in industries remain absence. More efforts for prospective applications are required. For this reason, the influence of acid concentration on the yields of hemicellulosic and cellulosic sugars from sugarcane bagasse and the formation of furfural and HMF in a microwave irradiation environment will be explored in the present study. Particular attention is paid to the pretreatment with low sulfuric acid concentrations and optimum operating conditions are suggested.

2. Experimental

2.1. Raw material preparation and standards

Bagasse obtained from Taiwan Sugar Corporation in Tainan, Taiwan, was selected as the raw material to be studied. The bagasse was dried in an oven with the temperature of 105 °C for 24 h to remove the moisture in the law material. Then, the dried bagasse was grinded and sieved to the maximum particle size of 40 mesh (=0.42 mm). Subsequently, the grinded bagasse particles were placed in sealed plastic bags and stored in a desiccator at room temperature until experiments were carried out. In this study, three standards of hemicellulose, cellulose and lignin, were also analyzed for comparisons; they were purchased from SIGMA (X4252), Lancaster (A17730) and TCI (L0045), respectively.

2.2. Reaction system

The schematic of the pretreatment system is demonstrated in Fig. 1 in which a gas supply unit, a heating and power controller unit, a reactor and a pressure control unit were included. In the gas supply unit, nitrogen was stored in a cylinder for leak test and system purge. The heating and power control unit consisted of a microwave oven, a thermocouple and a power controller. The microwave oven was operated at a frequency of 2.45 GHz and its maximum power was 900 W. The signal from the thermocouple was sent to the power controller for controlling power output. The current output from the power controller was fixed at 10A to prevent damaging the oven. The reactor was a vessel made up of Teflon with the volume of 625 ml (50 mm i.d. × 318 mm length). The vessel was covered by a stainless steel cap and only part of the vessel's volume (450 ml) was exposed to microwave irradiation. The pressure control unit was composed of a pressure control switch, a pressure gauge and a pressure valve. The pressure control switch was utilized for controlling the temperature (or pressure) in the reactor; the pressure gauge was used to monitor the pressure and the pressure valve was mounted at the end of pipe for safety.

2.3. Experimental procedure

In each experimental run, 10 g bagasse sample was mixed with 100 ml dilute sulfuric acid solution (25 °C) in the reactor. The