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Efficient extraction and recovery of xylan and lignin from rice straw using a flow-through hydrothermal system

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ABSTRACT

A flow-through hydrothermal system was developed to increase the recovery of xylan, the extraction of lignin and the subsequent enzymatic hydrolysis efficiency of rice straw. The impact of the operational parameters of several hydrothermal pretreatment process, such as temperature (170–220 °C), time (10–40 min) and flow rate (0–160 mL/min), on the subsequent enzymatic hydrolysis and the total sugar yield was studied. In comparison to a batch hydrothermal process, the flow-through hydrothermal process shows improved xylose recovery, lignin removal and total sugar yield. Additionally, the enzymatic hydrolysis efficiency of the pretreated rice straw showed enhanced with xylan removal regardless of changes in the pretreatment's temperature, time and flow rate. Furthermore, the optimal conditions for the flow-through hydrothermal pretreatment were 200 °C for 10 min at a flow rate of 160 mL/min, which resulted in the almost complete removal of the lignin from rice straw and gave a maximum total sugar yield of 84%.

1. Introduction

Lignocellulosic materials, such as agricultural, hardwood and softwood residues, are potentially viable sources of sugars for the production of biofuels (such as bioethanol and biobutanol) and various other valuable chemicals. Lignocellulosic materials are particularly attractive because they do not compete with food crops. An estimated 740–1111 million tons of rice straw are produced globally every year. Moreover, rice is one of the most important agricultural crops in Asia and developing countries in Asia produce 90% of the world's rice straw [1,2]. Therefore, rice straw is an attractive lignocellulosic material for producing biofuels and other useful biomass chemicals.

The major constituents of lignocellulosic biomass that are used for bioconversion are cellulose, hemicellulose and lignin polymers. These compounds are closely associated with each other to constitute the cellular complex of vegetal biomass, which makes it extremely resistant to microbial attack [3,4]. Therefore, in biomass processing, the primary goal is to disrupt and remove the cross-linked matrix of lignin and hemicellulose that embeds the cellulose fibers so that the cellulose is more accessible to enzymatic hydrolysis. This difficult process is generally referred to as pretreatment and plays an important role in the biomass refinery process. Thus, pretreatment is necessary to alter the structure of biomass and to enhance the enzymatic hydrolysis of celluloses into monosaccharides [5–9].

Several physical and chemical pretreatment methods are currently employed to overcome the recalcitrance of lignocellulose, increase enzymatic efficiency and improve the yields of sugars. These include dilute acid, ammonia fiber expansion, hot water, lime and organic solvent pretreatment technologies [8–12]. Among these techniques, hydrothermal pretreatment is an environment-friendly pretreatment process that accomplishes hemicellulose hydrolysis, lignin degradation, cellulose alteration and recovery of polysaccharides. This method does not require corrosion resistant reactors or chemicals and almost completely avoids producing toxic compounds. Therefore, hydrothermal pretreatment of lignocellulosic biomass has been widely studied, owing to its high efficiency and relatively low cost. For industrial applications, continuous or semi-continuous processes are preferred over batch systems [13–19]. For example, Wyman's research group [13–15] discovered that flow through systems removed more hemicellulose and lignin from corn stover than batch systems did. Additionally, Galia et al. [18] reported that a flow-through system achieved a biomass solubilization of up to 44.5 wt% on a dry basis, while a batch system stopped at 34.5 wt%, suggesting that mass transfer could be the rate-determining step in the solubilization of the constituent biopolymers. These studies show that flow-through systems generally provide more removal of hemicellulose and lignin from biomass than batch systems at the same severity factors.

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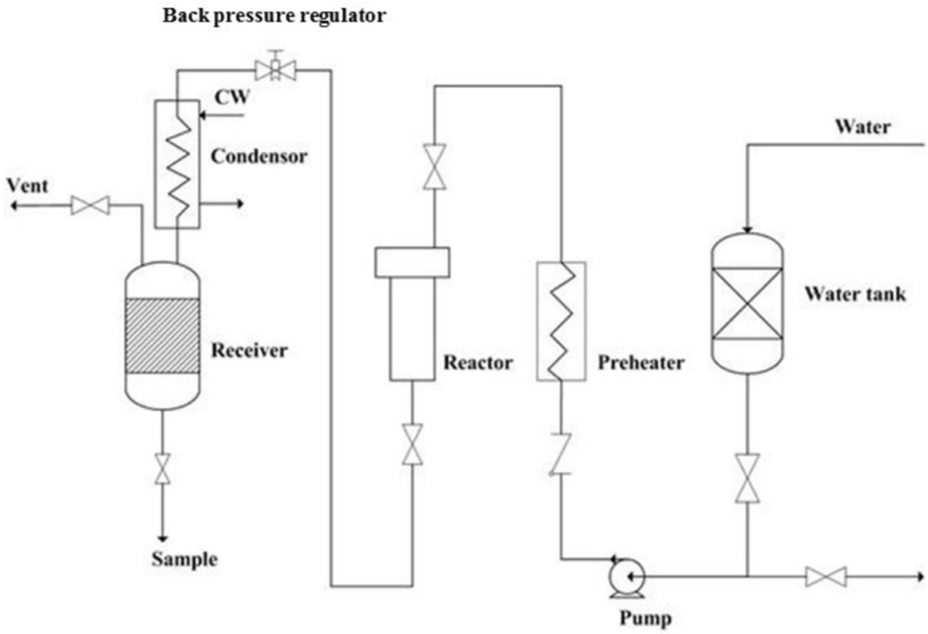

Fig. 1. Schematic diagram of the flow-through pretreatment system.

Using less inhibitor, such as furfural, in the efficient extraction of hemicellulose and lignin is a key issue during the pretreatment process. The goal of this study is to determine the temperature, residence time and flow rate for the flow-through hydrothermal pretreatment of rice straw that maximizes the hemicellulose (mainly xylose) recovery and total sugar yields. The total sugar yield was evaluated by estimating the xylose yield after pretreatment and the glucose yield from the subsequent enzymatic hydrolysis. In this study, the effects of xylan, lignin and cellulose content in the pretreated rice straw on the enzymatic hydrolysis efficiency are also reported.

2. Materials and methods

2.1. Biomass materials

The rice straw was primarily collected from private farms in Taiwan. The composition of the raw rice straw was as follows: glucan 32.9 ± 0.1%, xylan 18.7 ± 0.1%, arabinan 3.2 ± 0.1%, extractive 10.1 ± 0.2%, ash 11.3 ± 0.1% and lignin 19.1 ± 1.1%. The composition was calculated on a dry weight basis. Oven-dried rice straw was chopped into smaller pieces (~10 mm) and used as the raw material.

2.2. Pretreatment system and experiments

The flow-through system was modified for use with PARR Series 4530 2 L Floor Stand Reactors [20]. As depicted in Fig. 1, the system consisted of a water tank, a pump, a preheater, a high-pressure reactor, a condenser, and a receiver. The biomass in the high-pressure reactor was heated with electrical coil heaters that were in contact with the walls of the reactor, and cooled by an internal cooling coil that used tap water as the coolant. Moreover, the reactor was connected a reactor controller, which can control temperature and stirring speed, and it can be equipped to monitor a redundant temperature and pressure. The pressure was controlled by a back-pressure regulator installed at the hydrolysate outlet. All experiments were performed in the flow-through system. The 2 L reactor was charged with 25 g of dried rice straw (~10 mm) and 500 g of water at solid-liquid ratio of 5% (w/w). Then, the reactor with a blender stirring at 150 rpm was heated with electrical coil heaters and cooled by an internal cooling coil. The reaction time was defined as zero when the desired temperature (170–220 °C) was reached. At this time, the pump was turned on to pass hot water through the biomass at the desired flow rate (0–160 mL/min). When the target reaction time (10–30 min) was reached, the pump was turned off, and the reactor was immediately cooled.

As shown in Fig. 2, the obtained slurry was filtered to separate liquid and solid. The liquid is a xylose-rich hydrolysate and the solid is a cellulose-rich residue that was subsequently enzymatically hydrolyzed. The enzymatic hydrolysis was performed in 250 mL flasks using 50 mM sodium acetate buffer (pH 4.8) and 2% dry matter (w/w) at 50 °C on an orbital shaker at 100 rpm for 72 h The cellulase, Celluclast 1.5 L, was loaded at 20 filter paper units (FPU)/g of dry cellulose, which was supplemented with 15 IU/g of Novozymes 188 β-glucosidase. One unit of FPU is defined as the amount of enzyme required to liberate 1 µmol of glucose from Whatman no. 1 filter paper per minute at 50 °C. The goal of pretreatment is not only to remove xylose from hemicellulose but also to increase the rate of enzymatic hydrolysis of cellulose into glucose. Thus, it is necessary to estimate pretreatment efficiency by combining the total xylose and glucose conversion yields from both the pretreatment and enzymatic hydrolysis processes. The total sugar yield is defined as the sum of the xylose and glucose saccharification yields. The xylose and glucose saccharification yields are calculated by the following equations:

Xylose sugar yield (%)
= [(Xylose (g) released in pretreatment and enzymatic hydrolysis) / (Total xylose and glucose (g) in the rice straw)] × 100
Glucose sugar yield (%)
= [(Glucose (g) released in pretreatment and enzymatic hydrolysis) / (Total xylose and glucose (g) in the rice straw)] × 100
Total sugar yield (%)
= [(Xylose and glucose (g) released in pretreatment and enzymatic hydrolysis) / (Total xylose and glucose (g) in the rice straw)] × 100