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Hydrothermal treatment of rice straw for carbohydrate production

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ABSTRACT

This study focused on the effect of hydrothermal (HT) treatment at 180 - 210 °C for holding 0 - 15 min on the solubilization of rice straw and the changes of HT residue. The optimum treatment conditions for the highest solubilization and solid reduction of rice straw was 210 °C for holding 0 min. Under this condition, the extraction yield and total organic carbon (TOC) concentration of the HT liquid part were the highest, about 44% and 7850 mg/L, respectively. The dry residue showed that the HT conditions above 200 °C for holding a short time were more efficient, which was confirmed by FT-IR and the changes of surface morphology under microscope. The reactor headspace could be an important factor because HT treatment with a lower headspace (HTp210-0(15)) yielded more soluble carbohydrate under the test conditions. Also, energy input calculated based on the 1 ton removed hemicellulose (extraction yield) in the headspace experiments proved this finding.

Keywords: Lignocellulosic biomass; hydrothermal treatment; cellulose recovery; biomass digestibility

INTRODUCTION

Increasing energy usage and the rapid depletion of fossil fuels require renewable energy development to reduce pollutions generated by fossil fuels. According to the Energy Information Administration of the United States (EIA), worldwide energy demand will increase by 40% by 2040, reaching about 800 quadrillion British thermal unit, with the rising countries accounting for the majority of the demand increases [1]. Due to its use as a fuel and other value-added chemical production, biomass or biofuel has attracted increasing attention among the numerous renewable energy sources such as geothermal, hydro, wind, and solar [2]. The fact that lignocellulosic biomass makes up a large portion of plant matter makes it the most plentiful renewable resource on earth. It is a desirable feedstock for making chemicals and fuels since it is accessible and affordable. The three main components of lignocellulosic biomass are cellulose (40 - 50%), lignin (15 - 20%), and hemicellulose (25 - 35%). Rice straw's recalcitrant nature is one of the challenges for its biochemical conversion to bioethanol and methane. To convert biomass to biofuel, cellulose and hemicellulose molecules must be broken down into monomers or simple sugars. Rice straw fermentation is difficult in practice, which creates a significant barrier for lignocellulosic biomass in the bioconversion process [3]. In a sugar platform bio refinery, pretreatment is an important step in increasing biomass digestibility. Several criteria define the goal of any pretreatment procedure: (1) maximizing the final yield such as ethanol and other valuable products; (2) high amount lignin removal; and (3) reducing the formation of degradation products that can inhibit the action of produce biofuels [3, 4]. There are four main types of treatments, *i.e.*, physical, chemical, physicochemical, and biological methods in the hydrolysis of lignocellulosic biomass, and some of these treatment methods are very effective. Many chemical, thermal, and biological pretreatment procedures have been extensively researched to increase lignocellulosic biomass susceptibility to later enzymatic hydrolysis [5]. The use of water as the primary reaction medium with no other chemical additives makes hydrothermal pretreatment one of the most effective pretreatment techniques in terms of both practical and environmental considerations [6].

Hydrothermal (HT) processing of lignocellulosic materials has been studied under a variety of operational conditions in the past. HT treatment operating temperatures are typically between 100 and 230 °C, though higher temperatures can be used. The efficiencies vary depending on the applied temperature and time, which are co-related factors. Generally, 180 - 210 °C with a short holding time (1 - 15 minutes) can achieve the best sugar refinery [7, 8]. Some researchers suggested HT treatment with some chemicals such as acid and alkali addition. According to Imman *et al*. [9], the carbohydrate yield from HT treatment with acid and alkali were about 30 - 40% higher than that without chemical addition. However, adding chemicals is not regarded as environmentally friendly. The liquid to solid ratio (LSR) of solid concentrations can range from 2 to 100 (w/w), with the most typical values being around 10 [5]. The interaction between HT temperature and holding time has a significant impact on the selection of both the liquid and solid phases. It is widely assumed that HT treatment at a higher temperature for a short time will result in slightly better pentoses yield and less inhibitor formation [10, 11]. HT treatment at 200 - 210 °C for a short period is effective: When corn stover was hydrothermally treated at 210 °C for 0 and 10 minutes, more than 90% of the xylan was solubilized [12, 13]. One of the most critical aspects in the process economics of commercializing lignocellulosic biomass conversion is energy consumption. That's why energy balance analysis is very important. According to He *et al*. [13], HT pretreatment gained energy about 2741 MJ/t-rice straw when the process was performed at 150 °C for 20 minutes, which was 300 MJ/t-rice straw more compared to the methane production from no pretreatment group. In addition, the energy recovery from the HT and microwave pretreatment was 43 - 53% and 57 - 79%, respectively [14]. Many researchers investigated the HT treatment on various types of lignocellulosic materials, but there is little information about HT reactor head space's influence on sugar recovery. This research aimed to determine the suitable HT treatment conditions for rice straw to achieve digestible sugars which can be used for maximal ethanol production.

EXPERIMENTAL

Materials: In this investigation, rice straw was collected from a farm area in Tsukuba (Ibaraki-ken, Japan) and cut up into small pieces and then be air-dried. The air-dried rice straw particles were milled for the experiment, with particle sizes ranging from 0.27 to 0.56 mm. Before use, the milled straw was kept in a plastic container in the dark at ambient temperature. The original rice straw used in this study contains 92.56% total solids, 50.3% total carbohydrates, 27.8% lignin and 10.44% ash.

Apparatus and procedure:

In a 200 mL stainless-steel reactor, HT treatment was performed. Rice straw was treated at 4 temperature levels in the range of 180 - 210 °C for 0 min, 5 min, 10 min, and 15 min, respectively. The temperature in the HT reactor was increased at 12 °C/min on average, and the pressure was around 1 bar. In addition, when it reached the holding time, the heater was powered off, and a table fan was used to cool it. The average cooling rate was 2 °C/min.

Nine different HT treatment conditions were performed in this study, which were labelled as HT180-10, HT180-15, HT190-10, HT200-5, HT200-10, HT210-0, HTP210-0(5), HTP210-0(9), HTP210-0(15). The first six experimental tests were to find out the suitable HT condition, and the last three experiments were to check whether the reactor pressure had any influence on the sugar yield. The installed pressure meter was used to read the reactor pressure, which was around 1 - 2 MPa depending on HT conditions. The treated rice straw was centrifuged after HT treatment, and the solid HT residue was rinsed with distilled water. The pH value, total organic carbon (TOC), volatile fatty acids (VFAs), and total carbohydrate of the isolated supernatant were all measured. After being washed with deionized water, the solid residue from HT was dried at 105 ºC for 24 hours and used to calculate the total yield based on the weight difference [15]. For future usage, the pretreated dry biomass was packaged in plastic bags and stored in the dark.

Analytical methods: The National renewable energy laboratory (NREL) method was used to determine total solid (TS), volatile solid (VS), and calculate yield [15]. The concentration of total soluble carbohydrates was measured using the phenol sulfuric acid technique with glucose as reference [16]. A pH meter was used to determine the pH value. Individual VFA species in the liquid from rice straw during HT treatment was determined using gas chromatography with a flame ionized detector (GC-8A, Shimadzu Corporation, Japan). VFAs were calculated as the sum of acetic, propionic, iso-butyric, n-butyric, iso-valeric, and n-valeric acids. A TOC analyzer was used to determine the total organic carbon (TOC) of the HT liquid component (TOC-V CSN, Shimadzu, Japan).

The modified method was used to determine the amounts of lignin, cellulose, and hemicellulose in HT treated dry biomass [15, 17]. In brief, 0.3 g of solid residue was mixed with 3 mL of 72% w/w H_2SO_4 on a laboratory shaker for 4.5 hours at ambient temperature (25 °C). The solution was then diluted to 4% and hydrolyzed overnight to convert cellulose to glucose. The liquid and solid components were then separated using vacuum filtration, and the solid part was dried at 105 °C for lignin analysis. Acid-soluble lignin and total carbohydrate were determined in the separated liquid.

All the trials were done three times and the average results were presented. The structural morphology of HT treated biomass and the raw rice straw were observed by optical microscopy. The structural modifications during the HT treatment were also investigated using an FT-IR spectrophotometer.

The energy consumption was estimated according to Eq. 1 [13]. The rice straw disposal capacity was expected to be 1 ton in this study.

$$E_{HT} = m_{wa}\,\gamma_{wa}(T_{HT} - T_{at}) + m_{rs}\,\gamma_{rs}(T_{HT} - T_{at}) \qquad \textbf{(1)}$$

Where; EHT (MJ) is the heat consumption by HT reactor; mrs (t) is the disposal capacity of rice straw; mwa (t) is the water usage; γwa is the specific heat capacity of water (4.18 kJ/kg °C); γrs is the specific heat capacity of rice straw (1.67 kJ/kg °C); THT (°C) is the HT treatment temperature (180-210 °C in this study); Tat is the temperature of the environment (25 °C in this study).

The out wall of the HT reactor would be supplied with thermal insulation material if it were implemented in practice; however, heat loss through the reactor wall during the HT process was ignored in this study.

RESULTS AND DISCUSSIONS

Soluble products from HT treatment of rice straw: Changes of pH value and extraction yield: HT treatment is an effective approach for the solubilization of biomass because the breakdown of macromolecular components is temperature-dependent. The HT extraction yield and pH value of the liquid fraction from HT treatment are shown in Fig. 1. The extraction yield reflects the amount of all dissolved components, including dissolved hemicellulose, cellulose, lignin, protein and other soluble compounds. The extraction yield varied from 31% (HT180-10) to 44% (HT210-0), and it was slightly declined to 39% under HTp210-0(5). As can be observed from the findings, increasing the peak temperature helped dissolve rice straw.

The maximum extraction yield was achieved at 210 °C. Under this HT temperature, an additional experiment was conducted to check the influence of headspace pressure and it was adjusted by amount of straw. As the additional experiment`s result shows, the maximum HT treatment extraction yields were 44.3% in HTp210-0(15), 39% in HTp210-0(5), and 40% in HTp-210-0(9), respectively. This observation agrees with Yu *et al.* [22] who found that the soluble yield was ~ 36% under 180 °C for 10 minute, which could be a little bit increased (~40%) at 200 °C.

The pH values varied from 3.31 (HT200-5) to 4.31 (HT180-10). From Fig.1, the pH value was decreased from 4.31 to 3.31 (HT200-5), then slightly increased to 3.55 at HT210, probably due to a higher temperature especially > 200 °C can break down some organic acids [18]. Generally, when compared to the total extraction yield and pH value, a reverse tendency was noticed: the increased extraction yield was accompanied by a decreased pH value, probably owing to the production of organic acids from the dissolved hemicellulose.

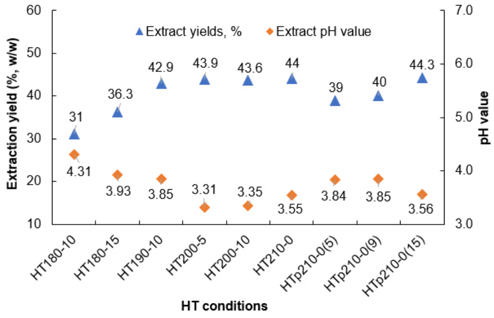

Fig. 1. Extraction yield and pH value of HT liquid fraction.

When the reactor headspace was changed, the pH values were also detected to change under 210 °C, which were degreased to 3.84, and 3.56 under HTp210-0(5) and HTp210-0(15), respectively. The results show that HTp210-0(5) and HTp210-0(9) conditions cannot substantially break down hemicellulose to organic acids when compared to HT210-0(15). This means that the reactor headspace or pressure may influence the extraction yield and the liquid pH value.

Dissolved carbohydrate and TOC from rice straw by HT treatment: The total dissolved carbohydrate was determined using the phenol-sulfuric acid method. This method can reflect all types of sugars such as xylose, glucose and others. Fig. 2 shows the production of total sugars in the liquid fraction from HT treatment, including monomeric and oligomeric sugars. The total carbohydrate concentration varied depending on the HT temperature and holding time. The lowest value was 8.3% from HT180-10, which was increased up to 17.1% under HT210-0. The total carbohydrate in rice straw is mostly made up of easily soluble polysaccharides (hemicellulose and mono sugar), rather than crystalline cellulose that is usually degraded at temperatures above 230 °C [19]. It means under HT210, the obtained dissolved total carbohydrate was mainly from the dissolved hemicellulose. Total TOC concentration in the liquid part of HT treated rice straw followed a similar pattern to total carbohydrate concentration. The lowest value was 4927 mg/L from HT180-10, and the highest

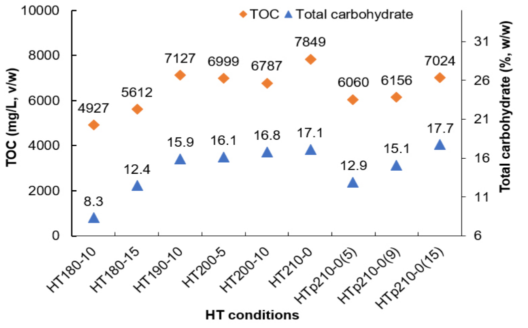

Fig. 2. Soluble carbohydrate production and dissolved total organic carbons (TOC) from HT liquid fraction.

value was 7849 mg/L obtained under HT210-0.

Based on the above results, the most suitable condition was determined as HT210-0, under which the highest carbohydrate yield and TOC were achieved. For the headspace experiment, the amount of total carbohydrate and TOC were lower in HTp-210-0(5) and HTp-210-0(9), when compared to HTp-210-0(15). More specifically, the total carbohydrates were 12.9% and 15.1% with TOC being 6060 mg/L and 6156 mg/L when the HT treatment was conducted under HTp-210-0(5) and HTp-210-0(9), respectively. In contrast, the total carbohydrate was 17.7% with TOC being 7024 mg/L under HTp-210-0(15). This observation also suggests that the reactor headspace effected on the extraction yield and liquid products.

Dissolved organic acids in liquid fraction from HT treatments: Under the hydrothermal condition, xylose molecules can be broken down with organic acid production, which can influence the liquid pH value [18]. The VFAs obtained by HT treatment of rice straw at the appropriate peak temperatures are shown in Fig. 3. The total concentration of VFAs was increased with the increase in HT temperature, while it was slightly degreased when prolonging the holding time. A longer holding time might break down some organic acids. The dominant acid was acetic acid from all test conditions, accounting for 43% or 333 mg/L in HT180-10 to 96% or 847 mg/L in HTp210-0 of the total VFAs in the HT liquid fraction. HT210-0 produced the most successful solubilization of rice straw of all the test conditions, mainly to the degradation of hemicellulose into xylose, which was then degraded into acetic acid.

Other VFA species were also detected. In the HT treatment liquid from HT180-10, there were 93 mg/L propionic acid, 95 mg/L n-butyric acid, 70 mg/L iso butyric acid, 83 mg/L iso valeric acid and 92 mg/L valeric acid. The concentrations of these VFAs were detected to decrease when the HT temperature increased over 200 °C.

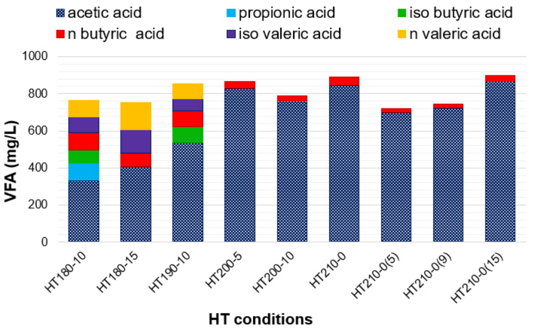

Fig. 3. Changes in individual volatile fatty acids (VFAs) during hydrothermal treatment of rice straw at peak temperatures.

Under HT200-5 condition, only two VFAs were detected, *i.e.*, acetic acid (829 mg/L) and n-butyric acid (37 mg/L), suggesting that a higher temperature is beneficial for VFAs decomposition.

In addition, a lower VFAs was detected in the liquid from HTp210-0(5) and HTp210-0(9) in comparison to HTp210-0(15). There were 3 noticeable unknown peaks from the gas chromatography results that need further confirmation by additional VFA standards. These unknown VFA products were observed to increase when HT treatment was conducted at temperature over 200°C. They could be levulinic acid and formic acid, which are produced at high temperatures from furfural and 5-HMF. This observation agrees with the statement by Liu *et al*. [20, 18] who detected the increase of these acids in the HT liquid part when temperature was increased to 200 °C. The effect of HT treatment on the solubilization of rice straw was studied. The HT treatment yielded various amounts of carbohydrate and other products from rice straw. HT210 was found to have a considerable impact on rice straw solubilization, boosting dissolved carbohydrate production with lower pH while also increasing VFA production. This observation suggests that this HT temperature is more suitable for hemicellulose decomposition from rice straw. The reactor headspace experiment found that a smaller headspace (HTp210-0(15)) is more effective compared to HTp210-0(5) and HTp210-0(9), yielding higher extraction rate, total carbohydrate and TOC concentrations.

Solid residue fraction from rice straw by HT pretreatment: Lignin and total carbohydrates: The solid fraction from rice straw by HT treatment was dried at 105 °C for 24 hours after being separated by centrifuge. This dry residue is important as it becomes a cellulose-rich biomass that could be used to produce ethanol and other useful products after hydrolysis. Fig. 4 shows the contents of lignin and total carbohydrate in the HT treated dry biomass. The lignin content was detected as 27.8 to 48 % (w/w) in rice straw and HT210-0, respectively. The breakdown of hemicellulose resulted in an increase in lignin content as the HT temperature goes up.

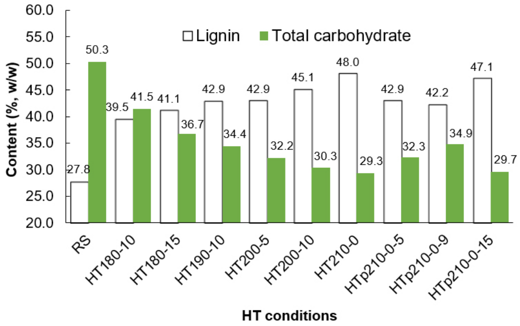

Fig. 4. Changes in lignin and total carbohydrate contents in the HT treated dry biomass.

Results show that HT210 condition can remove most of the hemicellulose. The total carbohydrates varied from 29.3 to 50.3%. The highest carbohydrate content was detected in the raw rice straw that contains all types of sugars such as hemicellulose, cellulose and soluble sugars.

The lowest total carbohydrate content was 29.3% in the treated dry biomass after 210 °C for holding 0 minute. This observation may indicate that much hemicellulose has been removed and the remained carbohydrate might be only glucose. Due to a lack of suitable conditions for the HPLC, the contents of xylose, glucose, galactose, and arabinose were not measured in this study.

The reactor headspace experiments also have some difference on lignin and total carbohydrate contents. The highest lignin content was 47.1% in HTp210-0(15) condition compared to other 2 conditions, indicating that condition is more efficient to decompose hemicellulose. However, the carbohydrates of HTp210-0(5), HTp210-0(9) were higher than HTp210-0(15) and they were 32.3%, 34.9%, respectively. It might be due to some amount of hemicellulose residue without breakdown. From the headspace experiments, amount of loaded sample including water should be greater than 80% of the reactor capacity. Under this condition, a higher pressure would be created to break down the lignocellulosic materials compared to the lower filled (like 50 - 70%) reactor.

Morphological changes of treated biomass: The morphological changes were observed by optic microscopy. The rice straw without treatment looks so smooth and without any significant damage. During the HT treatment process, the surface of the treated rice straw particles became more open, considerably rougher, and displayed clearly porous structures, likely resulting in much more contact between water molecules and carbohydrates inside the straw particles. The most suitable conditions were HT210-0 and HT200-10 because the smooth structure looked broken down.

FT-IR analysis: Under various HT treatment conditions, the FT-IR spectrum were recorded to investigate chemical structural changes in rice straw. As illustrated in Fig. 5, the changes in functional groups in the treated rice straw were particularly noticeable between the wavenumbers 600 cm^{-1} and 1800 cm^{-1}. The signal at 1720 cm^{-1}, corresponding to the C=O functional group, is a typical peak of ester connected acetyl, feruloyl, and ρ-coumaroyl groups between hemicellulose and lignin. The disappearance of this peak above 200 °C shows that HT treatment may have eliminated hemicellulose by cleaving the lignin-hemicellulose ester link. The signal observed at approximately 1432 cm^{-1} corresponds to -CH$_2$ bending of cellulose [21].

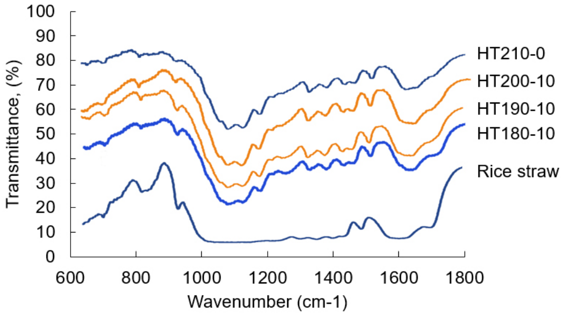

Fig. 5. FT-IR spectrum of original and treated rice straw.

The lignin-hemicellulose bond`s peaks at 1320 cm^{-1} (C-O of syringyl ring) and 1245 cm^{-1} (C-O of guaiacyl ring) were diminished in HT210-0. The peak at 1245 cm^{-1} (assigned to β-ether bonds in lignin and between lignin and carbohydrates [20] was declined in the FT-IR spectrum of treated rice straw above 200 °C. These observations support the chemical components and optical microscopy findings.

Energy consumption by HT treatment: The energy consumption by HT treatment is one of the important factors that influence the energy efficiency of the whole system. A higher HT temperature can easily break down the rice straw complex structure, while it may be economically infeasible when compared to lower temperature HT treatment in terms of energy efficiency. Energy input was calculated based on per ton of extraction yield, meaning how much energy was required for per ton of extract from HT treatment of rice straw. The energy input was calculated from the results obtained under HTp210-0(5), HTp210-0(9), and HTp210-0(15) in order to well understand the effect of the HT reactor headspace. Table 1 summarizes the required energy for per ton extract when HT treatment was conducted under the above conditions.

Table 1. The energy input of HT treatment for the headspace experiment

HT conditions	**Water used (ton)**	**Rice straw used (ton)**	**HT extraction yield (%)**	**HT yield (ton)**	**Energy input (MJ) for HT extraction**	**Energy input for per ton extract (MJ)**
HTp210-0(5)	5	0.5	39.0	0.195	4021	20620
HTp210-0(9)	9	0.9	40.0	0.360	7238	20104
HTp210-(15)	15	1.5	44.3	0.665	12063	18153

These data did not include the energy needed for drying after HT treatment. The energy consumption was calculated as 20,620 MJ, 20,104 MJ and 18,153 MJ by HTp-210-0(5), HTp-210-0(9) and HTp-210-0(15), respectively. The lowest energy was consumed under HTp210-0(15) condition due to its higher extraction yield than the other two HT210 conditions. This result also suggests that the HT reactor headspace is critically essential for the enhanced breakdown of rice straw when energy consumption is taken into consideration. However, a more detailed energy balance analysis is necessary when the final products such as ethanol, methane and other useful products are considered, which might be different when different final products being concerned.

CONCLUSIONS

In this study, we investigated the effects of HT treatment on rice straw solubilization and residue changes. In terms of achieving optimal results, the HT treatment conducted at 210 °C for 0 minutes yielded the best outcome, with a soluble carbohydrate yield of 44% and a total organic carbon (TOC) content of 17.1%. The temperature of HT treatment was found to exert a significant influence on the production of volatile fatty acids (VFAs), with acetic acid being the predominant species in this condition. Moreover, this study showed that HT treatment demonstrated higher efficiency at temperatures above 200 °C and short holding times, which was supported by evidence from FT-IR spectra and morphological changes. Furthermore, we observed that reducing the headspace in the reactor resulted in a more efficient recovery of carbohydrates from rice straw with lowest energy usage.

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