Influence of Alkaline Hydrothermal Pretreatment of Rice Straw on Biomass Composition

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Abstract – *Rice straw utilization for the production of fuel and other chemicals via fermentation route needs several pretreatments due to its compact structure between lignin and cellulose in the plant cell walls. It inhibits the decomposition of biomass by microorganism. In this study, rice straw was hydrothermally treated at different temperatures (100–200 °C) with (0-7%) NaOH addition to improve decomposition of biomass. This work demonstrated that the content of the lignin and hemicelluloses fractions was reduced with the increase of the hydrothermal temperature and NaOH content. The results of this study pointed out that hydrothermal treatment with NaOH addition can increase rice straw organic degradation as indicated by increasing delignification, hemicellulose solubilization and lower crystallinity index of rice straw. More lignin, cellulose and hemicelluloses were solubilized at higher severity factor. Thermogravimetric analysis showed that the rate of thermal degradation began at lower temperature for pretreated rice straw comparing to the untreated rice straw.*

Keywords – *alkaline-hydrothermal, cellulose, hemicelluloses, lignin, rice straw.*

1. INTRODUCTION

Consumption of energy derived from fossil fuels continues to increase, causing an energy crisis, increasing greenhouse gases and other environmental problems. Research to obtain renewable energy sources from biomass as a substitute for fossil fuels is important for the future energy provision. Biomass lignocellulosic material is very widely available throughout the world, so its utilization is very attractive to be a source of energy and chemicals [1].

Lignocellulosic constituents are mainly composed of lignin, cellulose and hemicellulose. Cellulose is a crystalline polymer mainly composed of glucose, hemicellulose is an interconnecting material which is branched heteropolymer and lignin is heteropolymer which is a combination of phenolic subunits providing tightness to the cell wall [2]. This complex structure in plants causes lignocellulose resistant to be degraded by enzymes from microoorganism and thus contributing difficulties in production of bioethanol, biogas or biohydrogen by fermentation route. Due to the difficulty of decomposition of lignocellulose, it is necessary to develop pretreatment technology to break the compact structure of lignocellosic material so that it will increase enzymatic digestibility by microorganisms [3]. Among these pretreatments, hydrothermal treatment is a process that could be further developed because it is environmentally friendly process, less corrosion and high energy efficiency [4], [5]. The hydrothermal treatment process can increase the biomass surface area and thus improve the accessibility of enzymes [6]. Previous study showed that temperature of hydrothermal process had been found to be the major effect on the pretreatment effectiveness towards producing highly digestible substrate [7].

Previous study on a laboratory scale conducted by Wang *et al.*, [8], showed that hydrothermal pretreatment of rice straw at 90 -120 °C for 10 minutes resulted in an increase in biogas production only 3% higher than that biogas from untreated rice straw. It was thought that toxic substance was formed during hydrothermal process. Another work by Chandra *et al.* [9] showed that NaOH treatment in rice straw increase biogas production by 132% higher than that of untreated rice straw.

In this work, hydrothermal pretreatment would be modified using alkaline condition by adding NaOH solution directly during hydrothermal process. Poisonous derivatives, such as phenolic compounds, furfural and HMF may be released during hydrothermal process and induce inhibitions in fermentation process [10]. The addition of NaOH will accelerate the degradation of lignin in rice straw and reduce poisonous substance so that the hydrothermal process was expected to be carried out at lower temperatures with smaller energy requirements. In this way, it was expected that the volume of product fermentation will be increased even further.

In this work, rice straw was hydrothermally treated with and without addition of alkaline NaOH. The structures of the obtained hydrothermal product were thoroughly characterized for its cellulose, hemicelluloses, lignin, sugar and furfural composition. In addition, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were also performed to expose the structural features and its relationship with thermal behaviors. From this study it will be able to characterize the effect of biomass composition on the next process for fermentation in biogas, biohydrogen or bioethanol production. Previous research on the production of biogas or biohydrogen from rice straw has not characterized the effect of ingredients product contained in the substrate from the hydrothermal process so that efforts can be established to optimize treatment results

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to increase biogas, bioethanol or biohydrogen production.

2. MATERIALS AND METHODS

2.1 Raw Material

Rice straw was collected from a local rice field in Sidoarjo district Indonesia. The biomass was sun dried and cut into pieces in size of 5 cm then stored in plastic bags without any additional treatment. The processed biomass rice straw was then used as a material for experimental studies. Finer size of rice straw was not required because in a previous study [11], mechanical pretreatment on reducing rice straw size of 5, 2, 0.5, and 0.2 cm did not show any significant increases in biogas yield. The native rice straw used in this study mainly contained of 25.4% lignin, 34.8% cellulose and 26.5% hemicellulose with ash content of 15.0%.

2.2 Hydrothermal Treatment

The hydrothermal treatment process was performed in an autoclave reactor made of 8 mm thick stainless steel, 20 cm in diameter and 65 cm in height with total volume of 13 liters. The reactor vessel was installed with PID temperature controller to ensure the temperature of hydrothermal process in operating condition and thermocouple to measure the temperature inside the reactor. The reactor contained one (1) kilogram of rice straw and 7 liters of water and alkali NaOH concentration of 0%, 3%, 5% and 7% (w/w dry rice straw). The NaOH crystal was dissolved into water to make a solution and added to one (1) kilogram of dry rice straw to keep 12.5% total solid concentration. The substrate was put into the autoclave reactor, sealed tightly and ready for hydrothermal process. The reaction temperature was co-heated to desired temperature for 50 to 60 minutes and maintained at desired temperature for 60 minutes. The temperature of hydrothermal process was 100, 120, 140, 160, 180 and 200ºC

After hydrothermal process, the solid fraction was separated, taken a little portion, washed with distilled water and dried for further measurement test. The liquid fraction was also separated for analysis of sugar and furfural as inhibitory by-products of hydrothermal process.

2.3 Analytical Methods

The composition of raw rice straw and pretreated rice straw was using DE method [12] for cellulose and hemicellulose content and TAPPI T222 method [13] for lignin content. The DE method is a gravimetric analysis of lignocellulosic constituent after being hydrolyzed or dissolved. The steps are: first, eliminating extractive content, then dissolution of lignin by sodium chlorite ($NaClO_2$) yielding solid holocellulose. Further dissolution using dilute hydrochloric acid would remove hemicelluloses and leave solid cellulose.

Solid yield was calculated as weight ratio solid product of hydrothermal process and rice straw in dry basis. Part of samples of hydrothermal products were taken and then separated from the liquid product. Solid products were then washed, filtered, oven dried and weighed. The weight of the samples was then compared to the weight of the raw rice straw in the samples.

The profile of reducing sugar in the hydrothermal liquor product were analyzed using DNS method [14] and the inhibitory by-products (furfural) in the liquid fractions from hydrothermal treatment were analyzed on a high performance liquid chromatograph, equipped with UV-Vis Detector using an Prominence (CTO-20A) Purospher® STAR C18 (250 mm x 4,0 mm, 5 µm) column operating at 30ºC with Acetonitrile : Water (5:95 v/v) as the mobile phase at a flow rate of 1 mL/min, injection volume of 10 µL and running time of 40 min.

Crystallinity determination of the native and treated rice straw biomass was done using X-ray diffraction (XRD), type of Phylips PW3050 equipped with software equipment APD (Automatic Powder Difraction) and using anode Cu tube at wave length of 1,54 À. The samples were scanned in a range of 2h = 10–30 with a step size of 0.02 at 500 kV, 30 mA and radiation at Cu Ka (k = 1.54 Å)**.**

Thermo-gravimetric analysis, TGA (TGN SDTA 851 Mettler Toledo) was performed for each sample hydrothermal treatment at rate of heating of 10°C per minute in the range temperature of 25°C - 900°C.

3. RESULTS AND DISCUSSIONS

3.1 Influence of Hydrothermal Treatment on Solid Composition

Figure 1 shows the solid yield from the hydrothermal process. From the chart, it can be shown that during the hydrothermal process some of the components in the straw will dissolve into water so that the amount of solids becomes reduced. Figure 1 also shows that the temperature and NaOH content during the hydrothermal process play an important role in dissolving the components of rice straw biomass. The higher the temperature and NaOH content in the hydrothermal process, the more components will be dissolved into the water. The lowest solid yield of 58%, was obtained at 200ºC and 7% NaOH by weight of dry rice straw.

The chemical compositions after hydrothermal process of rice straw biomas such as cellulose, hemicellulose lignin and are presented in Figures 2 to 4. As the treatment temperature increased, pH values decreased (data not shown). The acetyl groups in lignin and hemicelluloses may undergo a hydration reaction leading to acidification of the liquor [15] and caused a drop in pH due to hydrothermal pretreatment. Previous work reported that 5% NaOH was added to maintain appropriate pH of the substrate suitable for fermentation process [9]. In the present study however, the pH of treated rice straw by hydrothermal process was kept to neutral by adding alkali solution directly before hydrothermal processes. NaOH would react with organic acid released in hydration reaction and thus neutralized the pH.

Cellulose content of rice straw was originally 35% before treatment, which increased to around 60% after hydrothermal treatment at NaOH content of 7% (Figure

2). In contrast, as the treatment temperature increased the hemicellulose content of rice straw decreased, which is in line with the works of Zhou *et al.* [16], especially at NaOH content of 5% an 7% (Figure 3).

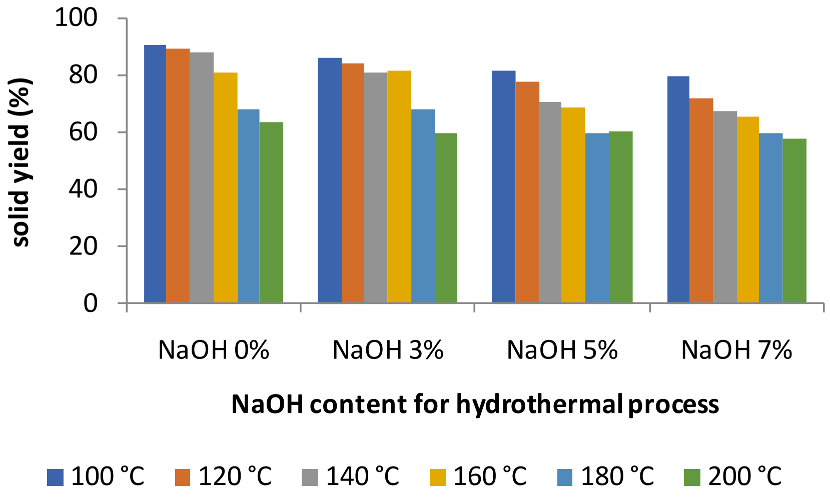

Fig. 1. Solid yield of alkaline hydrothermal process.

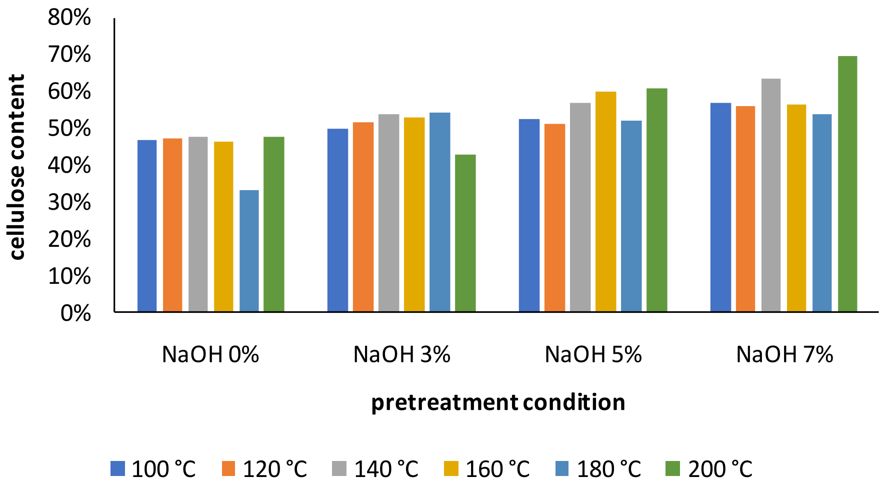

Fig. 2. Cellulose content of alkaline-hydrothermally treated rice straw on solid product.

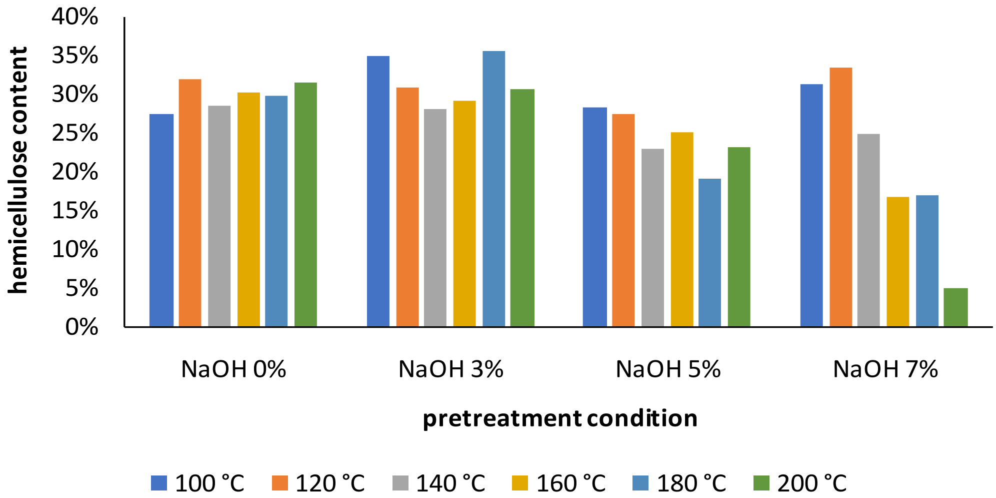

Fig. 3. Hemicellulose content of alkaline-hydrothermally treated rice straw on solid product.

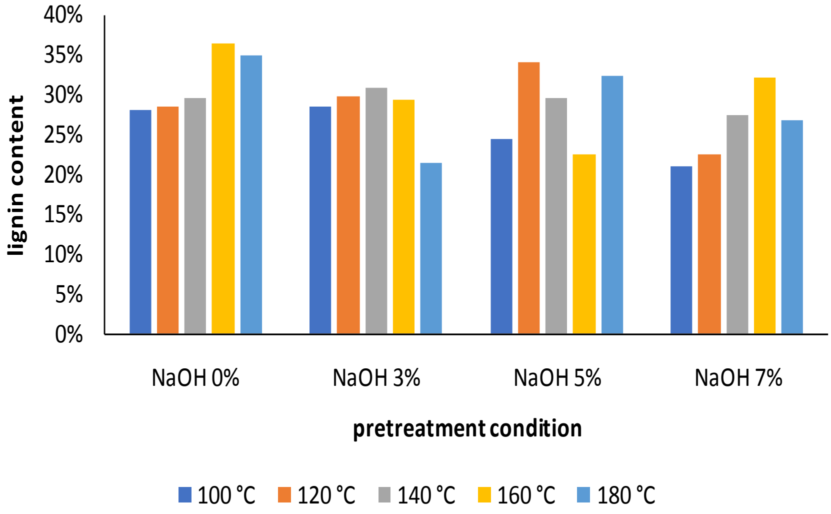

Fig. 4. Lignin content of alkaline-hydrothermally treated rice straw on solid product.

The hydrothermal process at low NaOH content (0-3%) has a fairly small effect on dissolving hemicellulose while at higher NaOH content (5-7%) the effect of NaOH content becomes very significant. Hydrothermal treatment with 5% NaOH content and temperature of 200°C, hemicellulose released from rice straw to 46% of the hemicellulose in the native raw rice straw, while at 7% NaOH content hemicellulose decreased to 80% of the initial hemicellulose content. During thermal treatment, hydronium ions were released due to autoionization and this conducted to hydrolysis of the biomass material. Hydrolysis process could lead to lignocellulosic decomposition and thus alter the lignocellulosic chemical constituent [17], converting the material into simpler compounds. Hemicellulose is the constituent which has the weakest bonding compared to lignin and cellulose so that it is widely reduced from rice straw solids during the hydrothermal process. Mechanism of hemicellulose solubilisation was given by Liu [15].

During the hydrothermal process, lignin is broken down into water-soluble products. This dissolution process is accelerated due to the reaction between phenol hydroxyl groups in lignin and NaOH [18] so that the remaining solids will contain more cellulose. Ran *et al.* [19] study obtained an increase of cellulose contents of 43% due to hydrothermal treatment of lignocellulosic biomass at 160°C. In conclusion, the properties of solid product of thermally treated biomass indicate that thermal pretreatment of rice straw leads to production of sugar or low molecular constituent as a result of hemicelluloses and lignin depolimerization and consequently increases its digestibility for microorganism due to degradation of hemicelluloses and lignin.

Different data were shown for lignin content in the treated rice straw. The content of lignin in the rice straw does not show a definite tendency to increase or decrease along with the operating conditions of the hydrothermal process (Figure 4). In hydrothermal process without the addition of NaOH (0% NaOH), lignin content shows an increase with temperature rise. This shows that degradation during the hydrothermal process occurs more in hemicellulose. However, hydrothermal processing as pretreatment caused re-localization of lignin on the surface of lignocellulosic biomass [20], thus microbe enzyme accessibility to the lignocellulosic biomass structure in the pretreated rice straw is favoured, and thus increasing the cellulose degradation potential. During hydrothermal process, hydroxyl bond in the lignin structure disappeared because of reaction of phenol hydroxyl with NaOH [18]. The reaction with NaOH makes lignin content lower than the lignin in the initial untreated rice straw. However, the heating during the hydrothermal process makes a lot of hemicellulose dissolved into the water, this makes the lignin content in the solids of the hydrothermal processed rice straw slightly change, especially at 7% NaOH where the level increases with the increase in treatment temperature.

The relations between the effect of temperature and duration of treatment on biomass is usually expressed in terms of severity factor. Many studies have carried out hydrothermal treatment, direct steam injection and steam explosion not only with addition of NaOH or other bases but also with the addition of acids to increase the efficiency of pretreatment efficiency with a lower severity factor in hydrothermal. The effect of acid on the severity factor was assessed by Chum *et al.* [21] which was later used to investigate the effect of bases on pretreatment by Silverstein *et al.* [22]. In this calculation, severity factor by combining time, temperature and acid or base concentration refers to Equation 1 below:

$$M_0 = t \times C^n \times \exp\left(\frac{T-100}{14.75}\right) \quad (1)$$

$$\text{severity factor} = \log(M_0) \quad (2)$$

where t is the residence time (min); M_0 is the modified severity parameter; C is the chemical concen-tration (wt%); T is the reaction temperature (°C); n is an arbitrary constant, assumed for first order reaction $n = 1$.

Figure 5 shows the relationship between severity factor and the materials dissolved in the water during the hydrothermal process. The dissolved material content was calculated as the difference between the weight of the initial component in raw rice straw and the weight in the hydrothermal pretreated rice straw. Figure 5 shows that the higher the severity factor, the more the amount of cellulose, hemicellulose and lignin dissolves in the water. The highest increase was in hemicellulose, followed by lignin and cellulose as the lowest. Hemicellulose was the most affected by severity factor because this component is the most easily degraded, while lignin has a strong bond of carbonyl in the aromatic ring [18] so that even with the NaOH addition in the hydrothermal process, the effect of severity factor is still lower than that of hemicellulose. Cellulose component has a good crystal structure making it also more difficult to break down so that the effect of severity factor is the lowest compared to hemicellulose and lignin. Figure 5 also provides information that despite of lignin and hemicellulose which are most affected by hydrothermal treatment, cellulose also undergoes dissolution in water when thermal heating occurs.

Different results were obtained from previous work by Rajput *et.al* [23] who conducted hydrothermal treatment without addition of NaOH by which the cellulose dissolution in water were not so much. The addition of NaOH rise the cellulose dissolution effect so that it would be expected to increase biogas and biohydrogen production as the products of this hydrothermal treatment process were used for raw feed materials.

3.2 Index of Crystallinity

The lignocellulosic biomass contains cellulose fibers which have crystalline properties, while hemicellulose and other constituents are generally amorphous. The part crystalline region in cellulose will be more resistant to microbial enzymes and other chemicals while the part that is amorphous will be more easily digested by microbial enzymes. Analysis of degree of crystallinity would further shows the effectiveness of lignocellulosic biomass pretreatment. One of the methods for analyzing crystallinity of cellulose is XRD analysis. The experimental result of XRD analysis is shown in Figure 6. The figure shows that the treated rice straw encountered some changes of intensity in some angles. Based on this figure the crystallinity can be derived.

The equations used in the crystallinity index determination was using the following equation as described by Segal *et al.* [24]:

$$Cr.I = \frac{I_{002} - I_{am}}{I_{002}} \quad (3)$$

Where $Cr.I$ is the crystallinity index, I_{002} is peak intensity at crystalline region and I_{am} is peak intensity at amorphous region.

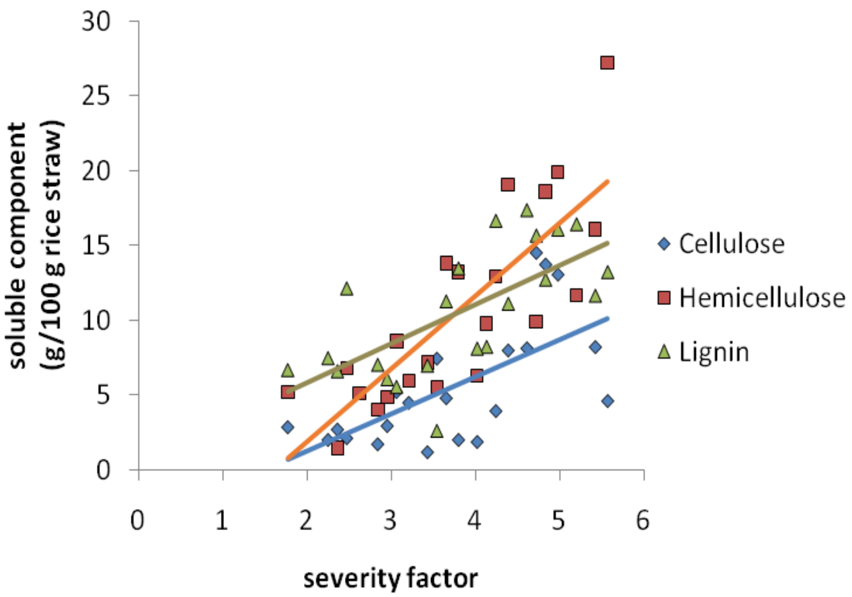

Fig. 5. Relation of degradation of lignocelluloses with severity factor after alkaline-hydrothermal treatment.

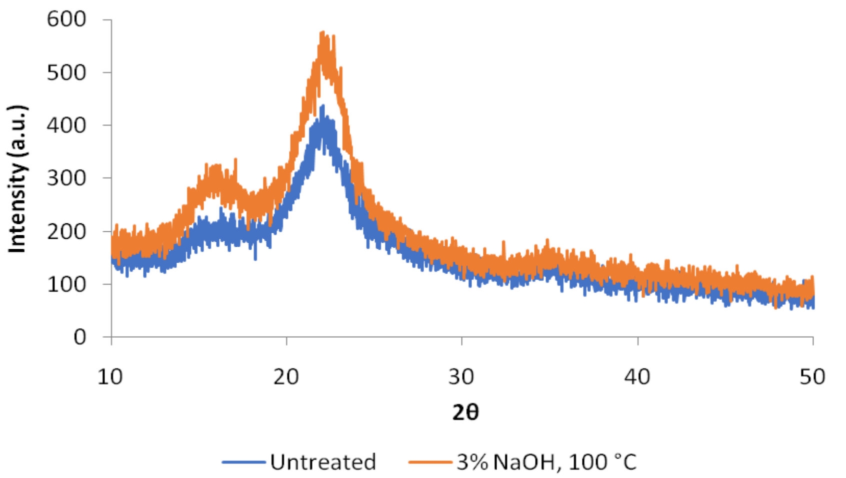

Fig. 6. XRD chart of rice straw before and after alkaline hydrothermal treatment of 3% NaOH at 100°C.

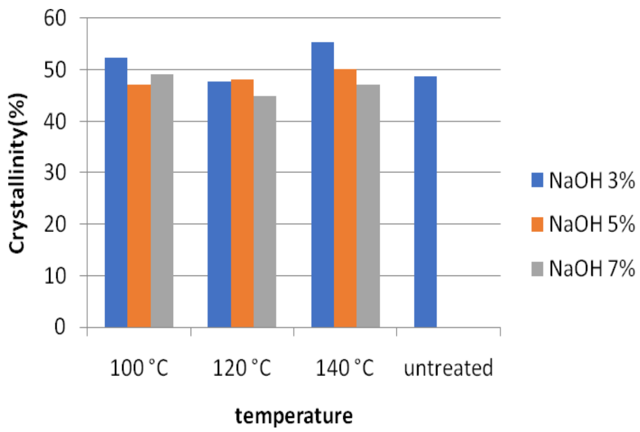

Fig. 7. Crystallinity Index of alkaline-hydrothermally treated and untreated rice straw.

The results of the crystallinity index of rice straw which has undergone the hydrothermal process are shown in Figure 7. With increase in treatment temperature, damage will occur to the structure of lignin and hemicellulose and finally changes in the structure of lignocellulose crystals which crystallinity index are shown in Figure 7. At temperature NaOH content of 3% hydrothermal treatment produced an increase in the crystallinity index of rice straw and at NaOH content of 7% there was a decrease. In case of no pretreatment, the strong bonds structure between lignin, cellulose and hemicellulose will reduce the ability of microbes to convert biomass into chemical products during fermentation process. However, in the case of pretreatment, hemicellulose and lignin was partially removed and this led to a change in cellulose accessibility [16] making the area of cellulose available for further biochemical processes.

The result of crystallinity index in this work seems to be opposite with previous studies [23],[25],[26] which stated that the higher the temperature of the hydrothermal process would increase the degree of crystallinity [23],[25] as well as increasing NaOH content would increase crystallinity [26]. The crystallinity in this work tends to decrease with increasing temperature and NaOH content. In previous studies hydrothermal pretreatment was carried out without the addition of NaOH and alkaline process was without heating while in this study the hydrothermal process was carried out with addition of NaOH.

Alkali utilizations as a promoter in hydrothermal process causes a more significant change in the nature of biomass compared to non-NaOH hydrothermal processes. At NaOH content of 5 and 7%, the higher the temperature, the lower the degree of crystallinity. Figure 7 shows that the effect of NaOH addition shows a significant effect of reducing crystallinity as well as transforming the chemical structure of biomass. This decrease in the degree of crystallinity can be attributed to the removal of hemicellulose and lignin which results in a reduced shielding effect and the opening of additional pores in the biomass structure. NaOH would be more easily penetrated into biomass structure because more pore is open and dissolve cellulose into the liquid, and this is accelerated at higher temperatures [27]. Figure 5 shows that cellulose is also dissolved during the hydrothermal process and tends to accelerate in higher NaOH content. Increasing the dissolved fraction of lignocellulosic biomass and decreasing the degree of crystallinity is expected to increase the penetration of enzymes which results in increasing product in the subsequent fermentation process.

3.3 Thermogravimetric Properties

Thermal stability is an important parameter for its use in the production of chemicals from lignocellulosic materials [28]. Thermal decomposition of lignocellulisic biomass is a very complex reaction, in which several chemical reactions occur simultaneously [29]. To understand the thermal behavior and structural features relationship of the biomass solids product of the alkaline hydrothermal treatment, the thermogravimetric analysis was applied in this work. Figures 8 to 9 shows the TGA and DTG curves from hydrothermally treated rice straw at 140°C.

The thermal degradation temperature range of lignin lies between 200-700°C, cellulose is in the temperature range of 250-350°C and hemicellulose is in the temperature of 200-300°C [30]. The biomass product in this study has the highest peak thermal degradation curve in the temperature range of 300-330°C, each of which is related to cellulose and lignin because the degradation of this temperature range between cellulose and lignin are coinciding. The relative intensity of the peak may be related to the content of cellulose and lignin and the strong bonding between the two of biomass constituent [31].

Figure 9 shows that the maximum decomposition temperature of untreated rice straw is higher than that of hydrothermally treated rice straw even though the maximum thermal decomposition rate is the highest. This result shows that the treatment process has changed the lignocelluloses structure of biomass in rice straw to begin to degrade thermally at lower temperature. As shown in Figure 9, the DTG peak is shifted to a lower temperature for higher NaOH content. The same results are also shown at other treatment temperatures (data not shown). At a higher pretreatment temperature, the difference between the peak temperature of thermal degradation between untreated and treated rice straw will be more evident.

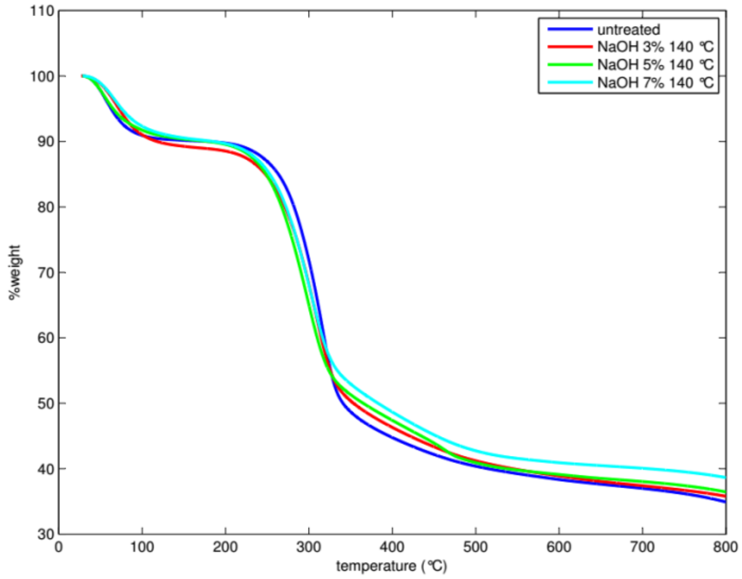

Fig. 8. TGA curve for alkaline-hydrothermally treated rice straw at temperature of 140 °C.

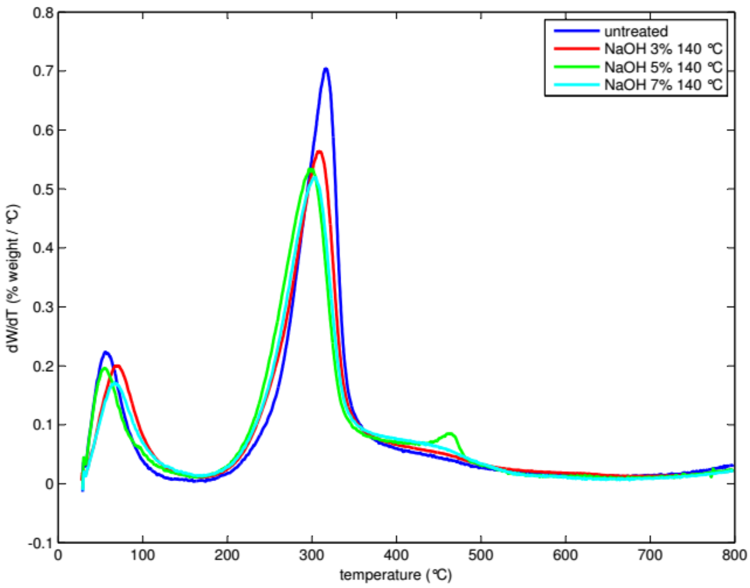

Fig. 9. DTG curve for alkaline-hydrothermally treated rice straw at temperature of 140 °C.

Figure 9 shows the peak of the DTG curve is lower for alkaline hydrothermally treated rice straw. The hydrothermal process had caused part of the lignin and hemicellulose constituent dissolve into the liquid which resulted in more cellulose remaining in the solid which decreased the rate of thermal degradation, because cellulose is a crystalline component which is more difficult to be degraded thermally.

3.4 Formation of Inhibitory Material (furfural)

Hydrothermal treatment of rice straw results in degradation of the biomass component into furfural. Furfural was produced from the dehydration reaction of sugar in the liquid fraction produced by hydrothermal operations. Figure 10 shows the profile of furfural concentration in the liquid fraction from treated rice straw. Maximum furfural formation was observed at a treatment temperature of 140°C and 5% NaOH. Base addition could cause furfural to be higher as a result of higher molecule depolymerization in lignin and hemicellulose. At treatment with higher NaOH content and temperature, more lignin and hemicellulose were hydrolyzed and dissolved into water as shown in Figures 3 and 4. Part of the dissolved material formed sugar which was then dehydrated to furfural. Imman *et al.* [7] found that glucose and pentose, which are hydrolysis product of cellulose and hemicellose, were removed as the main sugar from cellulose and hemicellulose hydrolysis in the treated rice straw and the maximum formation of HMF and furfural were observed at 140ºC, 0.5% NaOH for 20 minutes, which corresponds to the conditions of the highest observed glucan and xylan depolymerization.

Effect of NaOH content on efficiency and treatment selectivity was studied at high concentration (3-7%). Increased treatment temperature and NaOH content will result in an increased cellulose hydrolysis which leads to higher sugar content. The obtained increase in sugar content coincided with the increased accumulation of inhibiting products. It was observed at 140°C and 5% NaOH hydrothermal treatment yielded the highest furfural content (0.063 mg/mL). Lower concentrations of reducing sugar were found in the lower temperature and alkaline resulting in a lower furfural concentration.

Furfural plays an important role in the biogas or bioethanol productivity of due to the toxic nature of these substances. Furan concentration was present higher in the treatment process with higher alkaline content than that of lower content of NaOH, but the furfural concentration in this experiment was still below 2 mg/mL, which is the concentration threshold that inhibits microorganisms in the fermentation process of ethanol production [32].

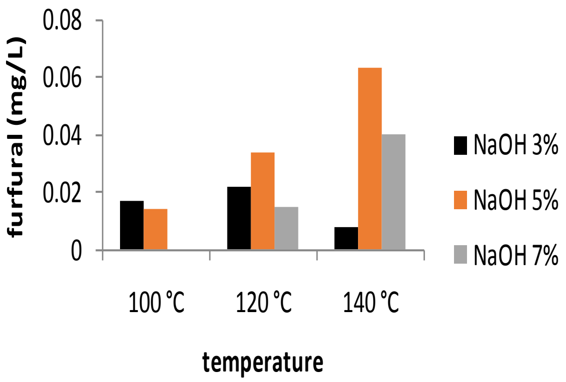

Fig. 10. Furfural concentration of liquid phase of treated rice straw.

4. CONCLUSION

In this study, effects of alkaline addition in hydrothermal treatment of rice straw were studied. It was found that the presence of NaOH on hydrothermal treatment has efficiently promoted as further fermentation route for fermentation of bioethanol, biohydrogen and biogas productions. Furthermore, hemicelluloses and lignin were efficiently removed from solid rice straw, resulted in a lower crystalinity index and low formation of unwanted by-products (furfural). The thermal properties data revealed that a lower rate of thermal degradation occurred for the treated rice straw. In conclusion, this works showed that feasibility of alkaline hydrothermal treatment of rice straw can accomplish further biomass conversion by fermentation in the production of biogas, biohydrogen or bioethanol.

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