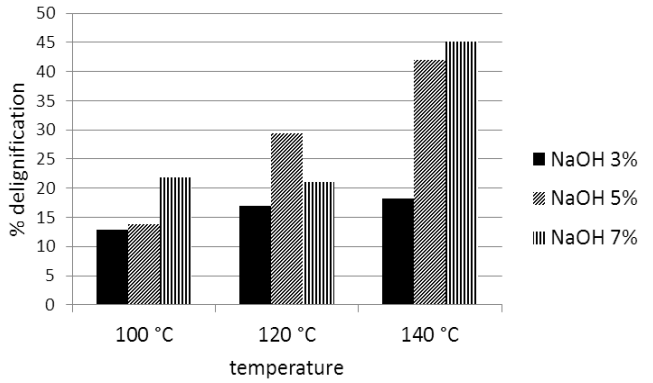

Fig. 4 Influence of alkaline concentration and temperature during hydrothermal treatment on delignification.

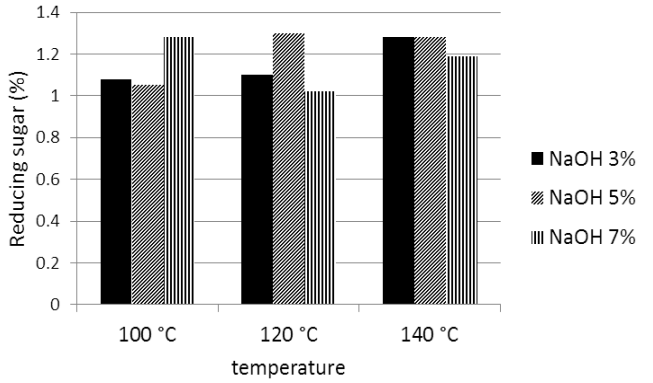

Fig. 5 Reducing Sugar concentration on the filtrate of hydrothermal treatment.

Reducing sugar is the most easily digestible component by microorganisms for biogas or bioethanol, hence this will play an important role in the productivity of biogas or bioethanol.

Cellulose crystallinity

Cellulose is a polymer with crystals and amorphous. The material contained in the crystal structure can be diffracted by X rays, so it can be used to find out the cellulose structure. The crystallinity index (CrI) is the ratio between the crystalline area and the total area of crystalline and amorphous. The amorphous compounds were removed during pre-treatment are lignin and hemicellulose, leaving the crystal fraction and raising the crystallinity index (Haque et al., 2012). The graph of XRD data analysis without treatment and after treatment at 100 ℃ with 3% NaOH concentration is shown in Fig. 6.

The XRD results from Fig. 6 shows the total crystallinity of all components contained in rice straw (cellulose, hemicellulose, lignin, and more). Some of the XRD graphs are seen to be similar to the XRD results of the pure cellulose (micro crystalline cellulose) reported by Yusnica *et al*. (2014) in Fig. 6, indicating that cellulose is a major component of the rice straw.

The equations used in the Crystalline Index determination by using the area area method (Poletto et al., 2012) are as follows:

$$Cr.I = \frac{A_{\text{crist}}}{A_{\text{total}}} \quad (1)$$

Cr.I= crystalisation index
A_{cryst} = The total area of the crystal
A_{total} = Total area of crystal and amorphous area

Summary of crystallinity index (*CrI*) before and after pre-treatment are shown in Fig. 7. From Fig. 7, it can be seen that the index of crystallinity of rice straw decreased after hydrothermal treatment. The effect of NaOH concentration at 100 ℃ on the crystallinity index (CrI) is seen to increase with the increase of NaOH concentration, while at 120 and 140 ℃ tends to decrease with the increase of NaOH concentration. Decrease in the index of crystallinity is indicated due to dissolved cellulose during the treatment process.

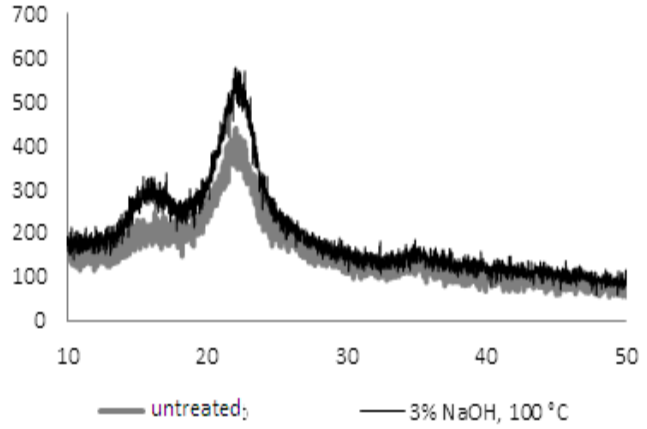

Fig. 6 XRD chart of rice straw before and after hydrothermal treatment of 3% NaOH 100 ℃.

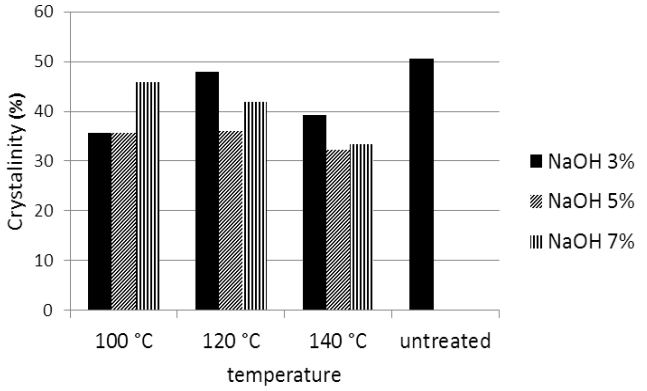

Fig. 7 Crystallinity Index before and after hydrothermal treatment.

The decrease in the crystallinity index (CrI) causes the degradability of rice straw to rise. This is due to the decrease of crystals in rice straw after hydrothermal treatment. The unchanged XRD pattern of cellulose crystals in rice straw before and after treatment was due to the fact that the treatment with NaOH only penetrated the crystal and amorphous surfaces, resulting in the swelling between the crystal areas (He et al., 2008). Meanwhile, in a research conducted by Bali et al. (2014), a treatment using 2% NaOH concentration and temperature 120 ℃ for 60 minutes resulted in a fluctuation of CrI.

Formation of inhibitor material (furfural)

Hydrothermal treatment of rice straw resulted the degradation of sugar in the product in the liquid fraction to form furfural (0.008 – 0.063 mg / mL furfural). Fig. 8 shows the chart of the furfural concentration of the liquid from treated rice straw. Maximum furfural formation was observed at a treatment temperature of 140 ℃, 5% NaOH, which corresponds to the condition with the highest observed yield on depolymerization producing sugars. The addition of bases lead to higher sugar yields in the hydrolysis of solids. Imman *et al.* (2015) found that glucose and pentose were removed as the main sugar from cellulose hydrolysis and hemicellulose in the treated rice straw. Higher NaOH concentration were observed to reduce glucose yield. Elevating NaOH content may cause the loss of sugar from glucan hydrolysis into monomer sugars and other degradation products.

Effect of temperature on efficiency and treatment selectivity was studied at high temperatures (100-160 ℃). Increased treatment temperature results in increased cellulose hydrolysis with higher concurrent glucose in the liquid phase. The resulting increase in sugar content with temperature coincided with the increased accumulation of inhibiting products.

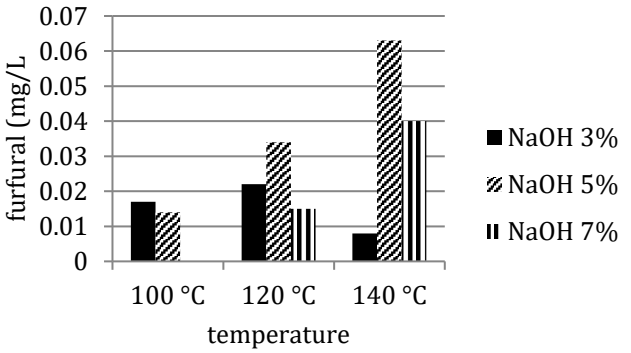

Fig. 8 Furfural concentration on treated of rice straw.

The highest furfural content (0.063 mg / mL) was observed at 140 ℃ using 5% NaOH. Lower concentrations of sugar degradation were found in the presence of lower base and temperature.

Furfural plays an important role in the productivity of biogas or bioethanol due to poisonous properties of this substance. The trend of furan formation of sugar degradation was observed from further degradation of monomer sugars under the acidic environment (Ertas *et al*., 2014). The accumulated concentration of furan present in a higher alkaline treatment process than in the absence of NaOH. It also showed that the furan compound decreased with increasing concentration of NaOH (from 5% to 7%) in the temperature range of 140 ℃. This could be due to the promotion of furan condensation reaction by NaOH (Amarasekara *et al.*, 2013). But the furfural concentration was still below 2 mg / mL, which is the threshold of inhibition for ethanologens (Sanchez *et al*., 1998). Therefore, direct fermentation of pre-hydrolyzates is feasible for further conversion to biofuels or chemicals via fermentation routes.

Thermogravimetric analysis (TGA)

The result of TGA analysis for treatment of rice straw at temperature of 140 ℃ is shown in Figs. 9 and 10. The analysis under non atmospheric conditions was performed to evaluate the pyrolytic behavior of the biomass curve. The TGA results showed that the devolatilization process begins at 150 ℃ and the maximum weight loss occurs in the range of 200-350 ℃. Above 370 ℃, a sudden change in the TGA curve occured that leads to slower weight loss within the temperature range of 350-400 ℃. The evaluation of the weight reduction of the sample was carried out between the temperature of 120 ℃, i.e. at the end of the evaporation of water, and ended at 550 ℃, indicating that more than 70% by weight of the fly material was removed at this interval.

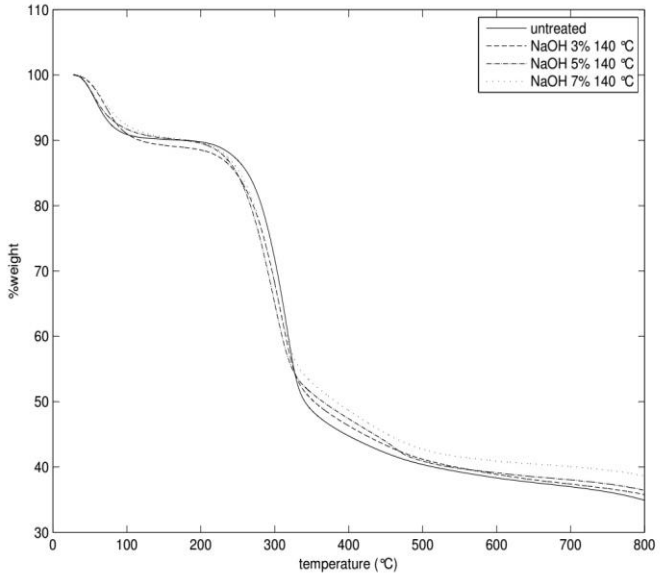

Fig 9. TGA curve for treated rice straw at temperature of 140 ℃.

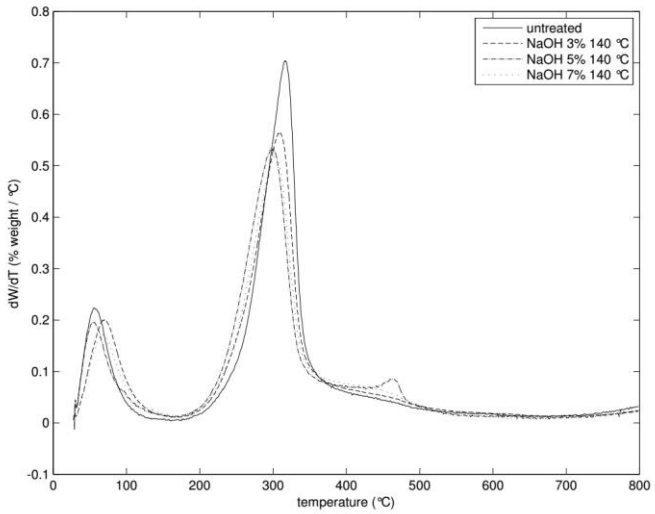

Fig. 10 DTG curve for treated rice straw at temperature of 140 ℃.

Fig. 10 shows the thermogravimetric differential curve (DTG) obtained from treated and untreated rice straw. The biomass curve produces three major peaks of biomass pyrolysis:, hemicellulose in the 200 -300 ℃ temperature range; α-cellulose in the 250- 350 ℃ range; and lignin in the 200-500 ℃ range. The relative intensity of the peaks might be related to the global content of hemicellulose, cellulose, and lignin present in biomass.

The DTG curve shows the presence of hemicellulose and cellulose in high proportions. In addition, the presence of peaks at higher temperatures indicated traces of lignin in the sample. The DTG curve of hemicellulose and a-cellulose given by Carrier et al. (2011) shows a larger peak that corresponds to high concentrations. However, its peak presence in the 200-300 ℃ temperature range confirms that the hemicellulose was still considerable in the sample. The lignin DTG curve obtained from washable biomass after acid hydrolysis (Carrier, 2011) was known to break down slowly over a wide temperature range, thus forming a flat tail portion of the DTG curve.

CONCLUSION

The effect of NaOH as an external base on rice straw treatment was demonstrated in this study. It was found that the presence of NaOH enhanced the enzymatic hydrolysis of rice straw. Cellulose and lignin were removed from the solid residue and high sugar yields were obtained in the liquid phase. Hydrothermal treatment in alkaline condition resulted in the dissolvemnt of lignin and hemicellulose. The higher the temperature and the concentration of NaOH, the more lignin and soluble hemicellulose. Crystallinity of solid product of hydrothermal treatment also showed a lower crystalinity index at higher the temperature and concentration of NaOH. Thermal decomposition rate has also shown to be faster at lower temperature

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