International Journal of Current Science, Engineering & Technology
ISSN : 2581-4311
Original Research Article | Open Access | AMCT 2017 Malaysia | *Special Issue*

Studies on Alkaline Pretreatment of Sugarcane Bagasse and Rice Straw Hydrolysis for the Recovery of Reducing Sugar

Jia Yi CHIN[1,a], Siti Kartini ENCHE AB RAHIM[1,b*] and Norazharuddin Shah ABDULLAH [2,c]

[1]Department of Chemical Engineering Technology, Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP),Level 1, Block S2, UniCITI Alam Campus, Sungai Chuchuh, Padang Besar, 02100, Perlis, Malaysia.

[2]Structural Material Niche Area, School of Material and Mineral Resouces Engineering, Universiti Sains Malaysia, 14300 NibongTebal, Pulau Pinang, Malaysia.

[a]genevia.chin@gmail.com, [b*]sitikartini@unimap.edu.my, [c]azhar.abdullah@usm.my

ABSTRACT. Preliminary screening was performed to investigate the effects of different types of alkaline solution (2%, w/v NaOH and $Ca(OH)_2$) on total reducing sugar (TRS) recovery. The results showed that usage of $Ca(OH)_2$ yields higher TRS as compared to NaOH. Therefore, $Ca(OH)_2$ was chosen for further studies in this effort. One-Factor-A-Time (OFAT) approach was employed to determine possible optimum ranges of chosen independent variables (i.e., pre-treatment temperature, concentration of $Ca(OH)_2$ and reaction time). It is found that for both biomasses, rice straw gives the higher yield of TRS. The optimum temperature for rice straw and sugarcane bagasse are 70 °C and 80 °C, respectively. Increasing the concentration of $Ca(OH)_2$ and reaction time gives an overall negative effect on the yield of TRS.

Keywords: *Alkaline pre-treatment, sugarcane bagasse, rice straw, acid hydrolysis;*

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;

DOI: *10.30967/ijcrset.1.S1.2018.28-34*

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Lignocellulosic materials such as sugarcane bagasse and rice straw are largely produced in tropical countries. These lignocellulosic materials are largely waste, and if these waste materials are fully utilized, 205 GL of bioethanol could be annually produced from fermentable sugar obtain through pre-treatment and hydrolysis, globally [1]. The main obstacle in hindering the advances of widespread uses of lignocellulosic biomass as primary renewable energy source is the recalcitrant natural characteristics of these materials. Lignocelluloses are made up of three primary compounds; cellulose, hemicellulose and lignin, along with several minor inorganic materials. The cellulose microfibrils which lead to its formation of crystalline structure enable cellulose to become highly resistant to enzymatic action in nature. The presence of lignin also serves as a protective barrier against the attack of enzyme or acid. In order to obtain fermentable sugar from lignocelluloses, the crystalline structure of cellulose needs to be disrupted to increase the accessibility of chemical or enzymatic attack on the cellulose structure [2]. Chemical pre-treatment involving alkaline hydrolysis is one of the most efficient treatments in reducing crystallinity of cellulose compared to other pre-treatment method [3]. It involves the use of bases such as sodium hydroxide, calcium hydroxide (lime), potassium hydroxide and ammonia to break the ester and glycosidic side chain resulting in structural changes in lignin. The mechanism is said to be saponification of intermolecular ester bonds cross-linked with hemicelluloses and lignin [4]. The present research work aims to determine the optimal conditions of alkaline pre-treatment for two types of biomass waste i.e., sugarcane bagasse and rice straw.

2. MATERIALS AND METHODS

2.1 Biomass preparation. Rice straw samples were obtained from a paddy farm locally in Padang Besar, Perlis. Samples were collected on March, 2015. Sugarcane bagasse samples were collected from a local stall in Perlis where the juices from sugarcane were pressed. Both samples were dried in the oven at temperature 80 °C.

2.2 Alkaline Pre-treatment. Alkali pre-treatment was conducted by weighing 5 g of each biomass. A 1:20 solid to liquid loading ratio was used for all the alkaline pre-treatment. Conical flasks containing samples and chosen alkaline solutions were placed in a water bath where constant temperature was maintained. Two alkaline reagents were used, NaOH and $Ca(OH)_2$ with various concentrations. The best alkaline treatment, in terms of producing high yield of TRS was chosen for further experiments. Table 1 shows the parameters investigated in the initial pre-treatment study.

Table 1 Parameters investigated in pre-treatment studies

Parameter	Ranges
Temperature (°C)	60 °C, 70 °C, 80 °C, 90 °C, 100 °C
Alkaline concentration (w/v)	1%, 2%, 3%, 4%, 5%
Pre-treatment time (hours)	1, 2, 3, 4, 5

The pre-treated samples were separated from the pre-treatment solution by filtration. Samples were then washed extensively with distilled water to reduce the pH close to neutral (pH 7-8). Pre-treated solid residues were dried in an oven overnight at 80 °C before subjected to acid hydrolysis for sugar conversion. The difference in mass of sample before and after pre-treatment indicates the percentage of lignin removal.

2.3 Acid hydrolysis. Glucose conversion was achieved by subjecting the pre-treated samples to acid hydrolysis using 6% HNO_3 at 90 °C for 90 min. Filtration was done using filter paper to separate solid residues from liquid. Liquid separated underwent neutralisation by adding NaOH. The neutralised liquor was analysed for amount of total reducing sugar using DNS assay while the solid residues that had been washed until pH close to 7 were dried overnight in an oven until constant weight was achieved. All biomass and liquid samples were sealed and stored at 4 °C until further analysis.

2.4 Total reducing sugar determination. The neutralised liquor from acid hydrolysis was determined for their sugar content using DNS assay [5]. 2 mL of DNS reagent is added to 2 mL of liquor in the test tube. Mixture was heated for 15 min at temperature of 95 °C. After cooling to room temperature, mixture was measured at wavelength of 540 nm using Shimadzu Scientific UV-1800 UV-vis spectrophotometer. Total reducing sugar concentration was then obtained from the standard glucose calibration curve.

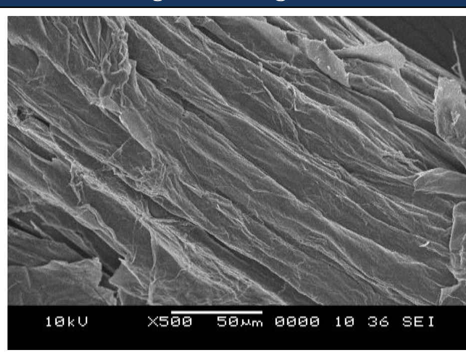
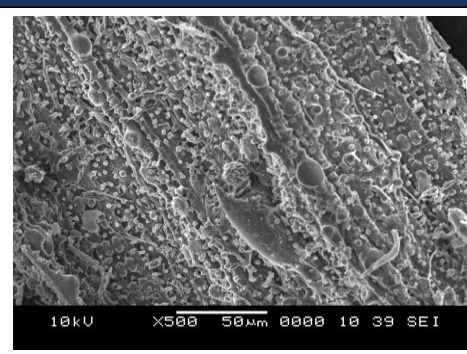
2.5 Scanning electron microscopy (SEM). Morphologies of both samples, before and after pre-treatment, were observed using SEM (JEOL JSM-6460LA). Pre-treated rice straw and sugarcane bagasse were sputter-coated with platinum. Scanning electron images that were obtained were compared.

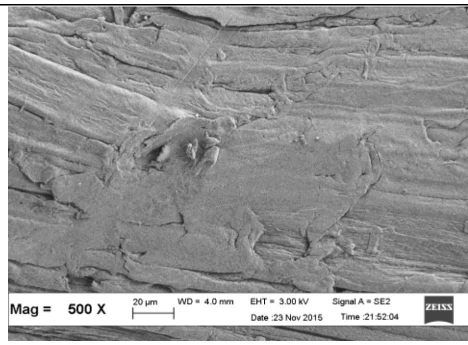
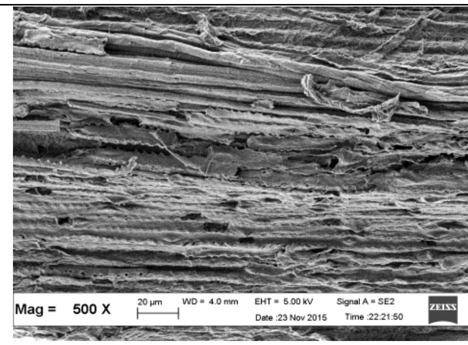
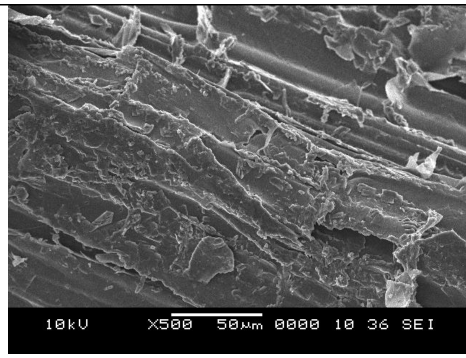
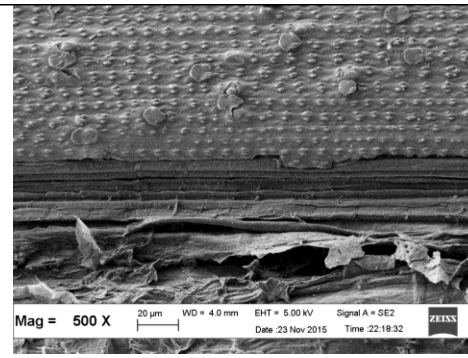
3. RESULTS AND DISCUSSION

3.1 Pre-treatment studies. SEM images were scrutinized to show the effect of pre-treatment on the structure and surface of samples. The surface structures of raw (before treatment) rice straw and sugarcane bagasse samples are seen in Table 2, images (a) and (b). Comparing those two images with images (c) and (d) together with (e) and (f), it is clearly shown that alkaline pre-treatment with NaOH and $Ca(OH)_2$, respectively, is effective. Significant morphological changes can be observed in comparison with the images of the samples of before and after pre-treated with both alkaline solutions. Under such comparison, it is hard to determine which pre-treatment solution is perhaps better. Thus, an analysis of the content of TRS in the pregnant alkaline solution is done.

Fig. 1 displays the yield of TRS for sugarcane bagasse and rice straw for both alkaline solutions. The results indicates that $Ca(OH)_2$ gives higher concentration of TRS in the pregnant solution than NaOH. This is especially true for sugarcane bagasse; a difference of nearly 2 g/L was observed if the two alkaline solutions were compared in terms of TRS concentration. Therefore, further studies of this work focuses on the usage of $Ca(OH)_2$ in pre-treatment, with relation to the effect of chosen operating conditions, i.e., temperature, $Ca(OH)_2$ concentration and reaction time.

Table 2 Morphology of raw material of sugarcane bagasse and rice straw, pre-treated with NaOH and pre-treated with $Ca(OH)_2$

Pre-treatment	Sugarcane bagasse	Rice straw
Without pre-treatment	 (a)	 (b)

Pre-treatment using NaOH	 (c)	 (d)
Pre-treatment using $Ca(OH)_2$	 (e)	 (f)

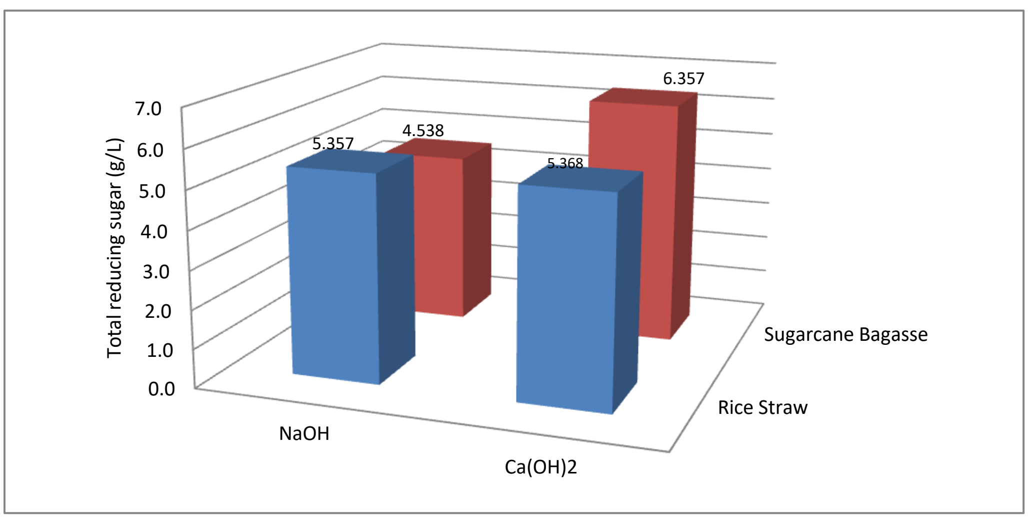


Fig. 1 Yield of total reducing sugar (TRS) with the effect of different alkaline solution choice with different biomass

3.2 Effect of temperature. Fig. 2 shows the overall TRS yield of sugarcane bagasse and rice straw with the effect of pre-treatment temperature. Generally, for both biomasses, TRS values initially increase along with pre-treatment temperature but then subsequently declined. This finding is agreeable with Idrees and co-researchers [6] and Sakdaronnarong et al. [7]. Mohd Shukri et al. [8], in their findings, mentioned that increase in pre-treatment temperature will cause increment in hemicellulose content; therefore, overheating at high temperatures of biomass burns the biomass surface. This result also was reported by Goh et al. [9], where in their findings, temperature did not significantly influence TRS recovery. In this study, it is observed that temperatures of 70 and 80 °C are perhaps optimum, for rice straw and sugarcane bagasse, respectively, to recover highest concentrations of TRS.

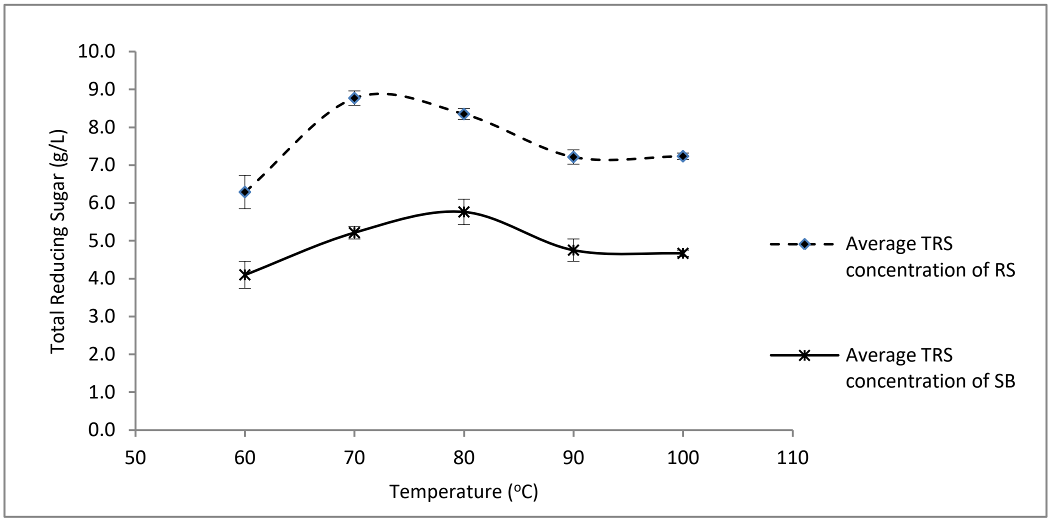


Fig. 2 Yield of total reducing sugar (TRS) with the effect of pre-treatment temperature for rice straw (RS) and sugarcane bagasse (SB)

3.3 Effect of $Ca(OH)_2$ concentration**.** The effect of $Ca(OH)_2$ concentration in the pre-treatment of both biomasses are shown in Fig. 3. For both samples, the concentration of TRS are seen rising with increasing $Ca(OH)_2$ concentration, up to 2% w/v. The increasing trend of TRS might be due to the lignin removal with the increased $Ca(OH)_2$ (alkaline) concentration from 1% v/w to 2v/w%. Rice straw was found to yield higher concentration of TRS. However, for both biomasses, the concentration of TRS started to drop when concentrations of $Ca(OH)_2$ increases above 2v/w%.

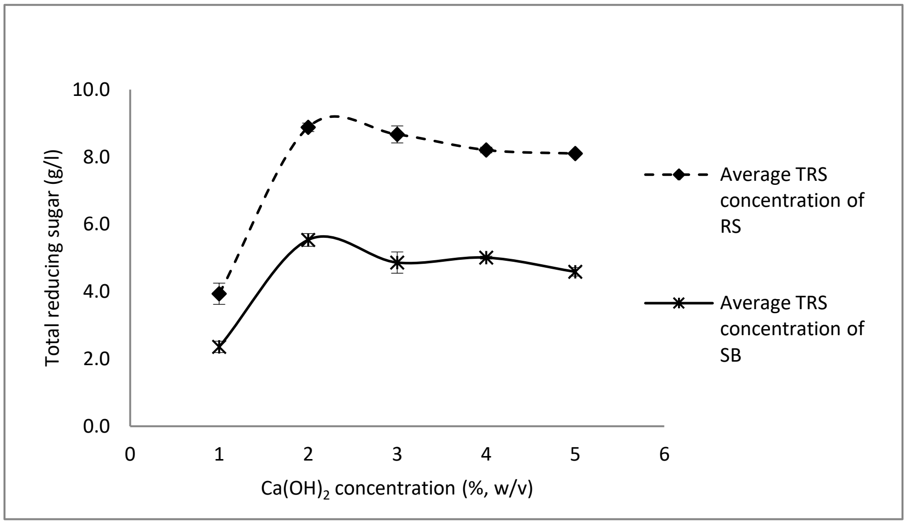


Fig. 3 Yield of total reducing sugar (TRS) with the effect of pre-treatment using different $Ca(OH)_2$ concentration for rice straw (RS) and sugarcane bagasse (SB)

3.4 Effect of reaction time. For both biomass samples in general, increasing the reaction time will increase the concentration of TRS. However, increasing the reaction time for more than 3 hours will give a negative effect on the recovery of TRS. This is because of longer reaction time might cause the initially exposed cellulose tends to be solubilized and degraded into furfural compounds. The presence of furfural and others inhibitors hinders the hydrolysis process to produce fermentable sugar [8].

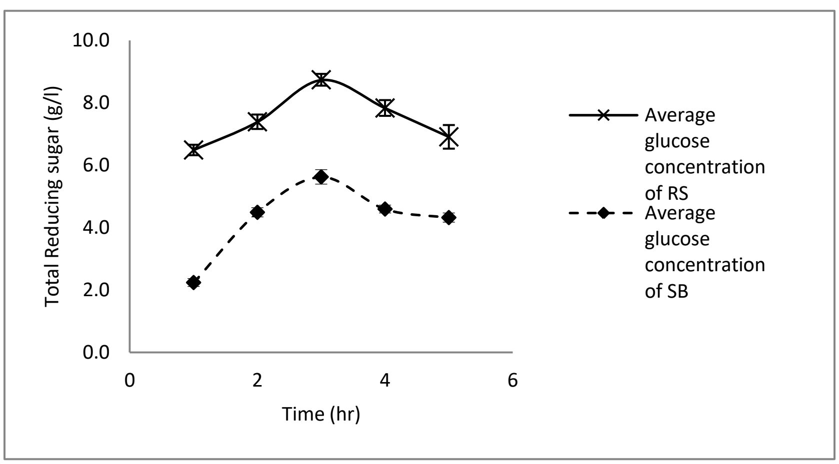


Fig. 5 Effects of residence time on sugarcane bagasse and rice straw from 1-5 hours. Pre-treatment conditions: respective optimum temperature found (70 °C for rice straw-RS, 80 °C for sugarcane bagasse-SB) with optimum alkaline concentration of 2% $Ca(OH)_2$)

4. SUMMARY

In this study, pre-treatment of sugarcane bagasse and rice straw were commenced using two chosen alkaline solutions. The results obtained show that $Ca(OH)_2$ gives higher yield of TRS. Further studies using that $Ca(OH)_2$ for both biomasses, reveals that TRS concentrations increases with pre-treatment temperature but then subsequently declined above 70 °C (for rice straw) and 80 °C (for sugarcane bagasse). Increasing $Ca(OH)_2$ concentrations and reaction time in pre-treatment process will increase the yield of TRS until 2v/w% and 3 hours (optimum condition). Increasing the conditions above these values, results in reduced TRS yield.

REFERENCES

[1.] S. Kim, B. E. Dale, Global potential bioethanol production from wasted crops and crop residues, Biomass Bioenergy, 26 (2004) 361-375.

[2] G. Brodeur, E. Yau, K. Badal, J. Collier, K.B. Ramachandran, S. Ramakrishnan, Chemical and physicochemical pretreatment of lignocellulosic biomass: a review, Enzyme Res., (2011) 787532.

[3] K. Mirahmadi, M.M. Kabir, A. Jeihanipour, K. Karimi, M.J. Taherzadeh, Alkaline pretreatment of spruce and birch to improve bioethanol and biogas production, BioResources, 5 (2010) 928-938.

[4] Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production: a review, Bioresources Technol., 83 (2002) 1-11.

[5] G.L. Miller, Use of dinitrosalicyclic reagent for determination of reducing sugar, Anal. Chem., 31 (1959) 426-428.

[6] M. Idrees, A. Adnan, S. Sheikh, F.A. Qureshi, Optimization of dilute acid pretreatment of water hyacinth biomass for enzymatic hydrolysis and ethanol production, EXCLI J., 12 (2013) 30-40.

[7] C. Sakdaronnarong, N. Srimarut, N. Lucknakhul, N. Na-songkla, W. Jonglertjunya, Two-step acid and alkaline ethanolysis/alkaline peroxide fractionation of sugarcane bagasse and rice straw for production of polylactic acid precursor, Biochem. Eng. J., 85 (2014) 49-62.

[8] S.S. Mohd Sukri, R.A. Rahman, R. Md Illias, H. Yaakob, Optimization of alkaline pre-treatment conditions of oil palm fronds in improving the lignocelluloses contents for reducing sugar production, Rom. Biotech. Lett., 19 (2014) 9006-9018.

[9] C.S. Goh, K.T. Lee, S. Bhatia, Hot compressed water pre-treatment of oil palm fronds to enhance glucose recovery for production of second generation bio-ethanol, Bioresources Technol., 101 (2010) 7362-7367.