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Lignin Removal from Sugarcane Leaves Lignocellulose using Sodium Hydrogen Sulfite as Glucose Enzymatic Hydrolysis Feedstock

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Abstract: Sugar cane leaves as an agricultural waste is the one of biomass that can be considered as an energy feedstock. Sugarcane leaves contain high cellulose that can be converted into sugars through some pretreatments and enzymatic hydrolysis. The glucose is then fermented into second-generation bioethanol. The existence of hemicellulose and lignin will decrease the efficiency of enzymatic hydrolysis.Dried sugar cane leaves crushed using a grinder (disc mill) and sieved to 60 mesh size and restrained passes 80 mesh, then dried in an oven to constant weight to remove water content. As raw material for this treatment, hemicellulose removal is carried out at a temperature 121^0C in an autoclave for 20 minutes with solid/acid ratio 1:26 and sulfuric acid concentration 2,2%. This step produces material with 12% hot water soluble, 7% hemicellulose, 32% cellulose, 48% lignin and 0% ash. The lignin removal uses Sodium Hydrogen Sulfite solution ($NaHSO_3$) pa from Merck.A raw material of 30 grams was mixed with 780 mL of sodium hydrogen sulfite solution in a stirred reactor for 30 minutes and 100 rpm. Variations conditions is the operating temperature (160, 170 and 180^0C) and sodium hydrogen sulfite concentration (8%, 9%, 10%, 11%, 12%). Sulfite pretreatment is affected by sodium hydrogen sulfite concentration and temperature. The optimum conditions which produce the largest lignin removal (79%) was obtained at 11% sodium hydrogen sulfite and 170^0C. Characteristics of high content cellulosic products from this stage is a cellulose powder with content of 80% cellulose, 3% hemicellulose and 10% lignin.
Keywords: sugarcane leaves, sulfite pretreatment, lignin removal, hydrolysis.

1. Introduction

Sugar cane leaves as an agricultural waste is the one of biomass that can be considered as an energy feedstock. Sugarcane leaves contain high cellulose that can be converted into sugars through some pretreatments and enzymatic hydrolysis. The glucose is then fermented into second-generation bioethanol. Another consideration is that bioethanol produced from biomass first generation had to be abandoned because of competition with foodstuffs such as palm oil, maize and cassava. The existence of hemicellulose and lignin will decrease the efficiency of enzymatic hydrolysis. The main limitation inhibiting the production of ethanol from agricultural waste is physical and chemical bonds between lignin and polysaccharides (cellulose and hemicellulose) in the cell wall and cellulose crystallinity. Lignin forms a protective layer coating cellulose and hemicellulose that prevent enzymatic degradation. The existence of hemicellulose and lignin will decrease the efficiency of hydrolysis so it is necessary to reduce the levels of these two components through set of pretreatment. Some research topics on biomass conversion of cellulose into sugar and/or ethanol with various raw materials pretreatment methods had been done. In this study, sugarcane leaves will converted to a high cellulose content material through acid and bisulfite pretreatment and maximize lignin removal through optimum conditions for concentrations variable of sodium hydrogen sulfite, the operating time and the ratio of sugarcane leaves to sodium hydrogen sulfite solution.

Akanksha conducted a study on the conversion of sorghum lignocellulosic biomass using sulfuric acid pretreatment to simplify the next enzyme hydrolysis process. Pretreatment studies wew done with sulfuric acid, followed by enzymatic hydrolysis. The efficiency of the process was evaluated on the basisof production of the total reducing sugar released during the process. The biomass that has been pretreated with optimized conditions (0.37% (v/v) H_2SO_4 at 16% loading sorghum at 150^0C for 15 minutes) can yield0.408 gram of reducing sugar per gram of pretreated biomass upon enzymatic hydrolysis for 48 hours at 20 FPU/g of 10% solid loading. This pretreatment partially removes hemicellulose and increase the hydrolysis efficiency up to 66.74%. The cellulose content after pretreatment at the optimum condition increased by 43.37%, while the hemicellulose content decreased by 34.26%. This process is effective and efficient for the mild operating conditions, directed hemicellulose hydrolysis and low inhibitor production[1].

Zhang uses wood fir with dilute sulfuric acid pretreatment (Diluted Acid/ DA) and sulfite pretreatment to overcome the barrier on lignocellulose (SPORL). Dilute acid pretreatment release almost all of hemicellulose, while SPORL at pH 4.5 removes significant amounts of lignin (20-25%). But both give digestibility enzymatic saccharification (Substrate Enzymatic Digestibility / SED) is low. DA gives SED value of 25-40% while SPORL gives SED value of 27%. The combination of both remove about 90% hemicellulose and 10-20% lignin with the SED value is 50-60%[2].

Anwar used rice husk was used as raw materials in pretreatment using dilute sulfuric acid. 1.5% solution of sulfuric acid at 100^0C for 30 minutes yield optimum results. The enzymatic hydrolysis produce16.52 mg glucose/mL, at 50^0C for 72 hours hydrolysis[3].

The production of cellulosic bioethanol from sugarcane bagasse and sugarcane leaves without enzyme hydrolysis process was studied. Pretreatment variables is performed by using hydrogen peroxide-alkali and sulfuric acid. The optimum operating hydrolysis was reached by 0.8 M sulfuric acid concentration for 24hourstirring, and 12 days fermentation for sugarcane leaves and 18 days for the bagasse. Ethanol produced from sugarcane leaves was 335.67 mg/ liter and from bagasse produce 395.5 mg/ liter of ethanol. Thongkhew[6] perform enzymatic hydrolysis of the substrate sugarcane leaves, after pretreatment with 3% sulfuric acid at a temperature of 35^0C for 48 hours and the concentration of enzyme 10 FPU/g substrate, produced 13.52 g/liter glucose[4,5].

Enzymatic hydrolysis of sugarcane bagasse (previously used hydrogen peroxide for delignification) was also done. Optimum conditions were obtained at temperature 50^0C, rawcellulase enzymes from Aspergillusniger, pH 4.8 for 120 hours. Reducing sugar produced was 54.47 mg/100 mL[7]. Betancur studied the production of bioethanol from bagasse through two majortreatment. They would find the optimum conditions of acid hydrolysis and the optimum conditions of fermentation. For1.09% (v/v) or 0.2 M acid concentration, the 1:2.8 (g:mL) ratio of solid:liquid, and 27 minutes hydrolysis time at 121^0C. This condition produces xylose at 50 g/L. The optimal fermentation time to produce 20 g/L of ethanol was 40 hours[8]. This method takes shorter time than Boopathy[5] research.

2. Experimental

Several main equipments were used is controlled reactor, hot plate magnetic stirrer, three-neck flask, oven dan furnace and standard glasswares. Sugarcane leaf was taken from the sugar cane plantations in the district Turen, Malang. Dried sugar cane leaves crushed using a grinder (disc mill) and sieved to 60 mesh size and restrained passes 80 mesh, then dried in an oven to constant weight to remove water content. Lignin removal pretreatment using sulfuric acid and sodium hydrogen sulfite pure analysis (pa) from Merck. This treatment will release the cellulose and hemicellulose from the lignin bind (delignification). Sulfuric acid solution can also dissolve hemicellulose. As raw material for this treatment, hemicellulose removal is carried out at a temperature 121^0C in an autoclave for 20 minutes with solid/acid ratio 1:26 and sulfuric acid concentration 2,2%. This step produces material with 12% hot water soluble, 7% hemicellulose, 32% cellulose, 48% lignin and 0% ash. The lignin removal uses Sodium Hydrogen Sulfite solution ($NaHSO_3$) pa from Merck. This treatment aims to dissolve the lignin that is still mixed with cellulose in the previous treatment. A raw material of 30 grams was mixed with 780 mL of sodium hydrogen sulfite solution in a controlled reactor for 30 minutes and 100 rpm mixing speed. Variations conditions is the operating temperature (160, 170 and 180^{0}C) and Solutions of sodium hydrogen sulfite concentration (8%, 9%, 10%, 11%, 12%). This process ran at controlled strirred tank reactor (Figure 1).

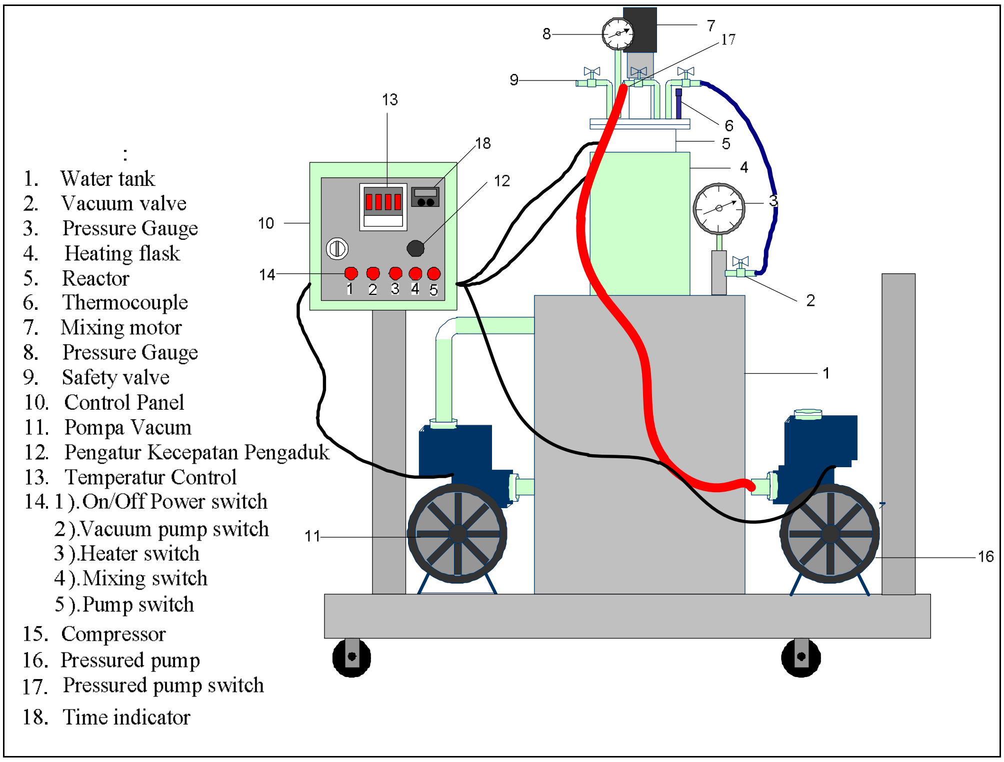

Figure 1. Stirred tank controlled reactor

3. Results and Discussion

As raw material for this treatment, hemicellulose removal is carried out at a temperature 121^{0}C in an autoclave for 20 minutes with solid/acid ratio 1:26 and sulfuric acid concentration 2,2%. This step produces material with 12% hot water soluble, 7% hemicellulose, 32% cellulose, 48% lignin and 0% ash. The lignin removal uses Sodium Hydrogen Sulfite solution ($NaHSO_3$) pa from Merck.This treatment aims to dissolve the lignin that is still mixed with cellulose in the previous treatment. A raw material of 30 grams was mixed with 780 mL of sodium hydrogen sulfite solution in a controlled reactor for 30 minutes and 100 rpm mixing speed. Variations conditions is the operating temperature (160, 170 and 180^{0}C) and Solutions of sodium hydrogen sulfite concentration (8%, 9%, 10%, 11%, 12%).

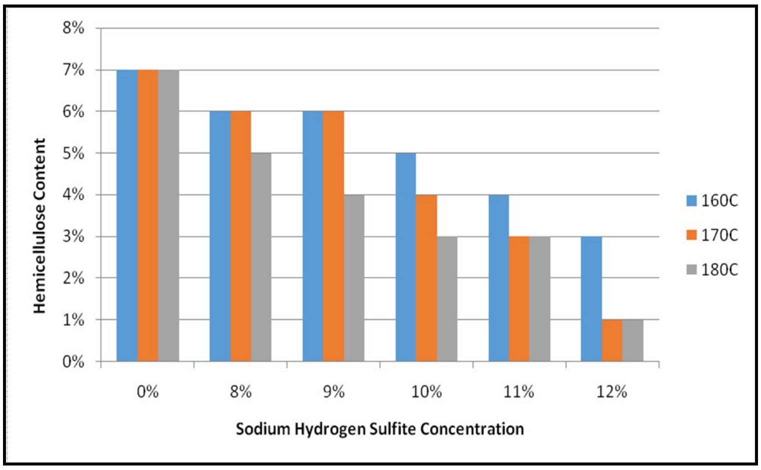

Figure 2.The effect of sodium hydrogen sulfite solution concentration to hemicellulose content

The effect of the concentration of sodium bisulfite solution to the hemicellulose content can be seen in Figure 2, which showed that hemicellulose levels for the sodium bisulfite pretreatment decreased although small enough (1%). This suggests that the hemicellulose slightly soluble in sodium bisulfite solution at a higher concentration (12%) and at a higher temperature (180^0C).

The main goal of this treatment is to reduce the lignin as much as possible. The effect of sodium bisulfite solution concentration and temperature of the lignin content in the product can be seen in Figure 3. This method was successful in reducing the lignin content significantly (up to 15%) at a concentration of 8% sodium bisulfite solution and achieve optimum results in the condition of 11% concentration of sodium bisulfite at a temperature of 170^0C. This is confirmed by an analysis based on lignin removal (Figure 3) which reached 80% at above optimum conditions. Lignin is not only physically dissolved in a solution of sodium bisulfite, but form a new compound sodium lignosulfonate which is soluble in sodium bisulfite solution. The greater the concentration of sodium bisulfite, the availability of reactants to combining with the greater lignin so as to dissolve the lignin in a significant amount.Tolbert calculating the average molecular weight of lignin from a variety of raw materials. Lignocellulosic sugarcane leaves is classifiedas softwood lignin having an average molecular weight of 5400 (an identical approach cane bamboo leaf). Lignin contained in the initial sample of 48% (equivalent to 14.4 grams and 0.003 gmol) while sodium bisulfite 11% (equivalent to 85.8 grams and 0.0825 gmol)[9]. Lignosulfonate compounds can be approximated by the structure shown in Figure 4, where the mole ratio of lignin and sodium bisulfite is 1: 3. The amount of sodium bisulfite solution used in this study exceeded this ratio. The greater the number one reactant, causing equilibrium moves toward the product so that more lignin can be separated.

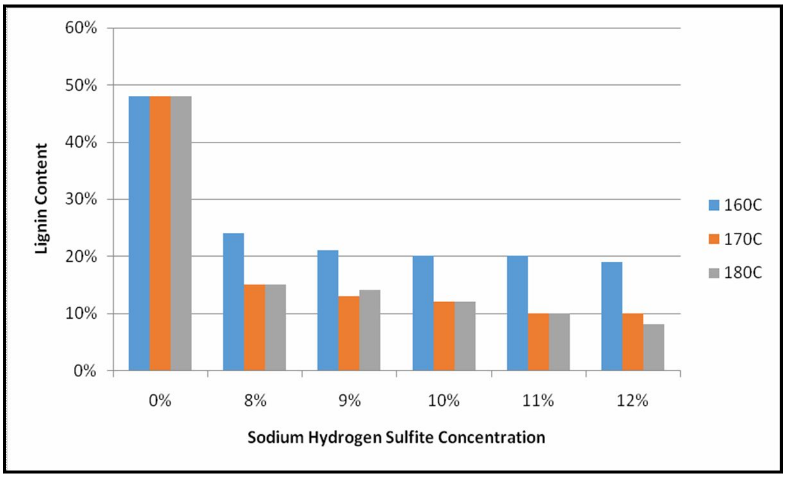

Figure 3.The effect of sodium hydrogen sulfite solution concentration to lignin content

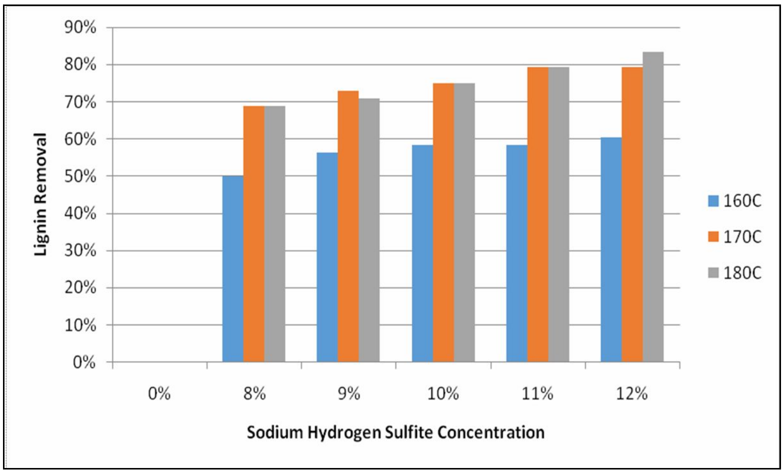

Figure 4.The effect of sodium hydrogen sulfite solution concentration to lignin removal

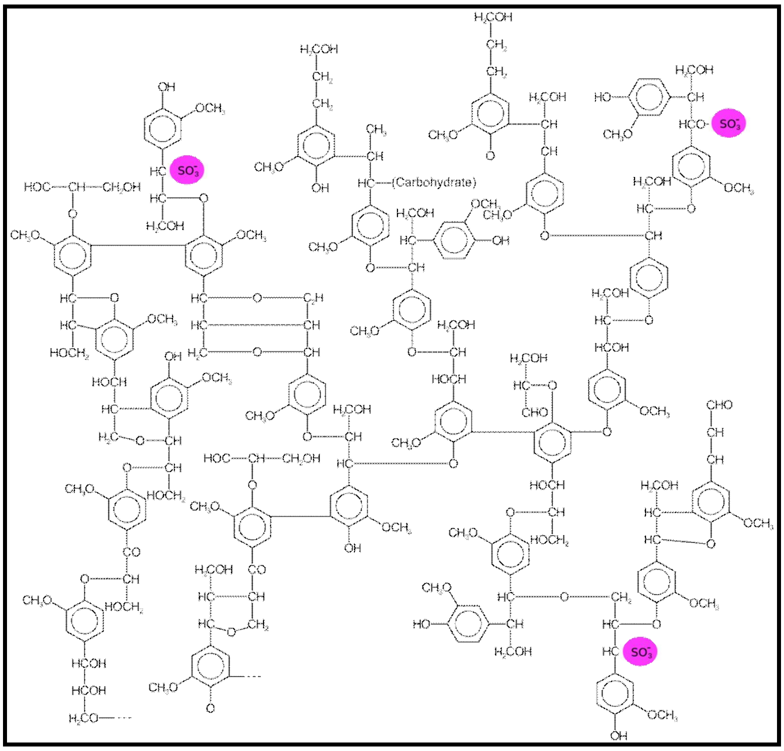

Figure 5.The approach of lignosulfonate structure

The effect of the concentration of sodium bisulfite solution to the cellulose content can be seen from Figure 6. The optimum conditions are taken is 11% sodium hydrogen sulfite concentration, operating temperature 170^{0}C that canremove 79% lignin. Sodium hydrogen sulfite at a concentration of 12% and 180^{0}C indeed produce higher lignin removal, but the increase is only 5%, then according to economic considerations, the previous conditions is more preferable. Characteristics of high concentrations of cellulosic products resulting from this stage is a cellulose powder with a content of 80% cellulose, 3%hemicellulose and 10%lignin.

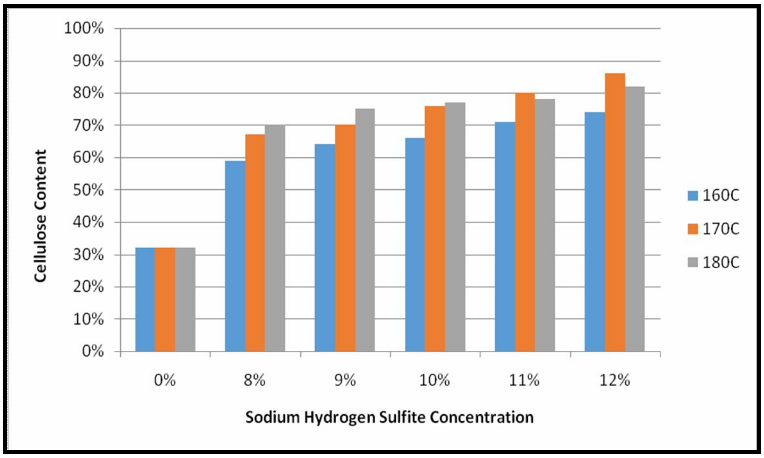

Figure 6.The effect of sodium hydrogen sulfite solution concentration to cellulose content

4. Conclusion

Sulfite pretreatment is affected by sodium hydrogen sulfite solution concentration and process temperature. The optimum conditions which generate the largest lignin removal (79%) was obtained at a concentration of 11% sodium hydrogen sulfite, the operating temperature of 170^{0}C. Characteristics of high concentrations cellulosic products resulting from this stage is a cellulose powder with a content of 80% cellulose, 3% hemicellulose and 10% lignin.

References

1. Akhanksha, K., A. Prasad, R.K. Sukumaran, M. Nampoothiri K, A. Pandey, Rao S S, P. Binod (2014). “Dilute Acid Pretreatment and Enzimatic Hydrolysis of Shorghum Biomass for Sugar Recovery-A Statistical Approach”. Indian Journal of Experimental Biology, Vol. 52, November 2014, pp. 1082-1089.
2. Zhang, Chao., Lei, Xiaochum., Scott, Tim.C., Zhu, J.Y., Li, Kecheng. (2013). ”Comparison Of Dilute Acid and Sulfite Pretreatment For Enzymatic Saccharification Of Earlywood and Latewood Of Douglass Fir”, Spinger Science and Business media New York
3. Anwar, Zahid., M. Gulfraz, M. Imran, M.Javaid Asad, A. I. Shafi, P.Anwar, R. Qureshi (2012). “Surface Methodology fo Bioethanol Production from cellulosic Biomass of Rice Polish”. Pak. J. Bot., 44(1) : 169-176.
4. Boopathy, R. and Dawson, L. (2007). “Use of post-harvest sugarcane residue for ethanol production,” Bioresource Technology 98, 1695-1699.
5. Boopathy, R. and Dawson, L. (2008). “Cellulosic Ethanol Production From Sugarcane Bagasse Without Enzymatic Saccharification.” Bioresource 3(2), 245-460.
6. Thongkheaw, S., Pitiyont, B. (2011). “Enzymatic Hydrolysis of Acid-Pretreated Sugarcane Shoot.” World Academy of Science, Engineering and Technology 60, 454-458.
7. Gunam, I. B. W., Wartini N. M., Anggreni A. A. M. D., dan Suparyana P. M. (2011). “Delignifikasi Ampas Tebu Dengan Larutan Natrium Hidroksida Sebelum Proses Sakarifikasi Secara Enzimatis Menggunakan Enzim Selulase Kasar Dari Aspergillus Niger Fnu 6018.” LIPI Teknologi Indonesia Vol.34, 24-32.
8. Betancur, Gabriel J. Vargas and Pereira Jr., Nei (2010). “Sugar cane bagasse as feedstock for second generation ethanol production. Part I: diluted acid pretreatment optimization.” Electronic Journal of Biotechnology, Vol.13(3).
9. Tolbert, A., Hannah Akinosho, RatayakornKhunsupat, Amit K. Naskar, Arthur J. ragauskas (2014).”Characterization and Analysis of The Molecular Weight of Lignin for Biorefining Studies”, Biofuels Bioproducts and Biorefining Review, Society of Chemical Industry and John Wiley & Sons, Ltd.

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