Optimization of Fenton Pretreatment Process for the Efficient Recovery of Reducing Sugar from Rice Straw

M.F. Tompang[1,*], B.B. Tan[1]

[1]Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia

[*]Corresponding author's email: fahrurrazi@unimap.edu.my

ABSTRACT: The lignin degradation of rice straw via the Fenton pretreatment process was investigated in mixed solvent of (dimethyl sulfoxide (DMSO)/water) as to evaluate the significant sugar recovery. A three-level Central Composite Design (CCD) was employed to evaluate the relationships between reducing sugar production and the process parameters (temperature, hydrogen peroxide and ferric chloride concentrations, and mixed solvent ratio) According to the statistical analysis, reducing sugar yield was 64.04% (w/v) from the optimized condition of 0.03 M of $FeCl_3$, 2.32 M of H_2O_2, and 18.11 vol% of DMSO/water. The filtrate from the pretreatment was directly applied to the enzymatic hydrolysis to compare the concentration of glucose produced from Fenton pretreated RS, commercial α-cellulose, and raw RS. Highest reducing sugar concentration (26.36 mg/ml) is found from Fenton pretreated RS, followed by α-cellulose (10.21 mg/ml) and raw RS (5.54 mg/ml). Hence, the modified Fenton pretreatment process is shown to be one of the best method for delignification of lignocellulosic biomass to enhance the recovery of reducing sugar as it provide simple and eco-friendly approach over other pretreament methods.

Keywords: *Sugar; Rice straw; Fenton reaction*

1. INTRODUCTION

RS consists of cellulose (35.2%), hemicellulose (26%), lignin (20%), and ash (18.8%) [1]. Open burning of RS emits greenhouse gas (GHG), and the deterioration of the soil-integrated straw leads to the rice disease [2]. Various studies for renewable biofuel resources were conducted to cope with the high demand for biofuel. Pretreatment permits the degradation of the lignocellulosic structure of RS, such as increasing the biomass's porosity and surface area [3]. The combination of the Fenton and organosolv pretreatment enhance RS's saccharification through Fenton reaction that increases the accessibility of free hydroxyl radicals to the lignocellulosic matrix for the high sugar recovery [4]. Optimization study was assisted by CCD in order to identify the optimized Fenton pretreatment conditions for further enzymatic hydrolysis of RS in improving the recovery of reducing sugars.

2. METHODOLOGY

RS was collected from the Ayer Hitam paddy field, Jerlun, Kedah, and cleaned before grounding and sieving to achieve a particle size smaller than 0.49 mm. A 50 ml of pretreatment reagent was made up of 1.5 ml of 0.03M of $FeCl_3$ in a 37.5 ml of 14.2 vol% of DMSO/water and mixed with 11 ml of 2.25 M of 35 wt% H_2O_2 in a beaker. The mixture was heated at 100°C and stirred at 60 rpm for 10 minutes before adding 0.2 g RS powder into 20 ml of Fenton reagent (pH 2) and heated at 90°C at 60 rpm for 10 minutes until the slurry was formed. The light brown residues from filtration were added into a 20 ml of new Fenton reagent at similar conditions as the first step. The reducing sugar from brownish-red filtrate was analyzed by DNS method at 540 nm prior to enzymatic hydrolysis [4]. A total of 19 trials from CCD was carried out by varying the temperature, the concentration of $FeCl_3$ and H_2O_2, and the volume of DMSO/water. Twenty ml of total filtrate with the highest reducing sugar content was added with 0.75 g of $CaCO_3$ (pH 4.8) and 0.183 ml of cellulase and stirred at 150 rpm for 24 hours at 50°C for the enzymatic hydrolysis before terminating the reaction at 85°C for 5 minutes. Controls consisting 0.19 g α-cellulose and 0.2 g raw RS were used as comparative substrates in enzymatic hydrolysis by maintaining the similar quantity of glucose content in sugar oligomer in filtrate (0.13 g) [4].

3. RESULTS AND DISCUSSION

3.1 Optimization of Fenton pretreatment conditions in a mixed solvent

CCD identified the highest glucose yield achieved after Fenton pretreatment, 64.71% at 90°C, 0.03 M of $FeCl_3$, 2.25 M of H_2O_2, and 14.20 vol% of DMSO/water. Figure 1 shows the 3D surface plot towards glucose yield based on the interaction between the parameters. As the temperature rose, the yield of monosaccharides during pretreatment increased. There was a possible formation of inhibitors such as HMF and furfural beyond 95°C that interrupted lignin degradation [4]. H_2O_2 initiated the Fenton reaction to form free hydroxyl radicals that remove lignin to enhance the efficiency of pretreatment [4]. However, beyond 2.35 M of H_2O_2, formed insoluble solids and possible formation of gluconic acid [5]. $FeCl_3$ is known as a hydroxyl radical scavenger; thus, beyond 0.32 M of $FeCl_3$ prevented reducing Fe^{2+} essential in forming hydroxyl free radicals [6]. The synergistic effect of $FeCl_3$ and H_2O_2 caused intensive destruction of the ether bond in cellulose and hemicellulose to form glucose along with the synergistic effect of DMSO/water, which accelerated at 14.2-25.0

vol% for deeper penetration of free radicals into the RS's structure to boost the yield of glucose by reducing the formation of inhibitors [4].

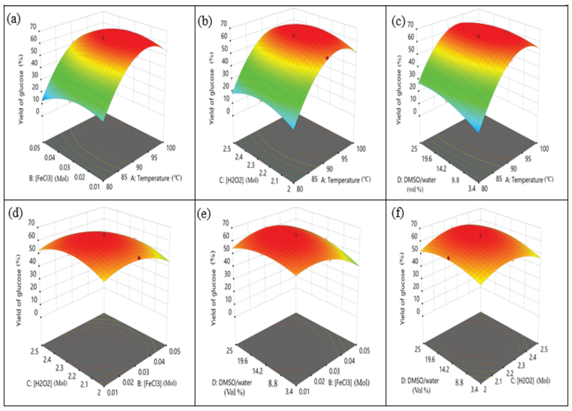

Figure 1. The 3D surface plot towards glucose yield: (a) temperature vs. [$FeCl_3$], (b) temperature vs. [H_2O_2], (c) temperature vs. the DMSO:water, (d) [$FeCl_3$] vs. [H_2O_2], (e) [$FeCl_3$] vs. the DMSO:water, (f) [H_2O_2] vs. the DMSO:water.

3.2 Comparison of glucose concentration via enzymatic hydrolysis using different sources of cellulose

Figure 2 depicts the comparison of the glucose concentration produced via enzymatic hydrolysis using three different sources of cellulose such as Fenton pretreated RS, α-cellulose, and raw RS. Similar result was recorded with study done by Yu et al. (2018), which the enzymatic hydrolysis of Fenton pretreated RS shown the highest yield of reducing sugar (26.36 mg/ml), followed by α-cellulose (10.21 mg/ml) and raw RS (5.54 mg/ml) after 24 hours at 50°C.

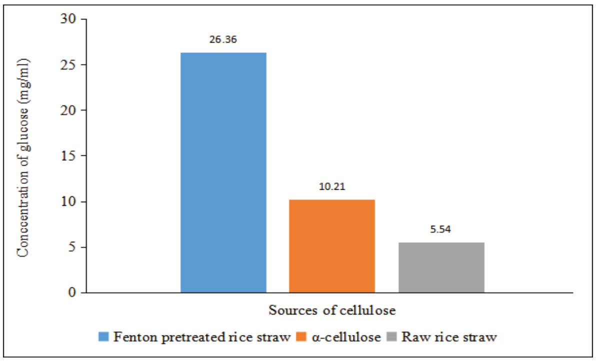

Figure 2. Comparison of glucose concentration from different sources of cellulose used in enzymatic hydrolysis.

These observations indicated that the Fenton pretreated filtrate, which contained $FeCl_3$, DMSO, and trace amounts of inhibitors, can be directly applied to enzymatic hydrolysis [4]. It was understandable when the efficiency of Fenton pretreated RS underwent enzymatic hydrolysis, which yields the highest glucose concentration compared to the others. This was because the soluble glucose oligomers produced after pretreatment were more accessible to cellulase than crystalline cellulose and the cellulose in raw RS, protected by lignin and hemicellulose [4]. Therefore, the Fenton reagent was an excellent choice in biomass pretreatment [7] compared to other pretreatment approaches.

4. CONCLUSION

The RSM based on CCD was used to optimize the conditions of the process parameters. The optimized conditions obtained were 95°C, 0.03 M of $FeCl_3$, 2.32 M of H_2O_2, and 18.11 vol% of DMSO/water for a maximum response of 64.04% of glucose yield. The comparison between the glucose concentration obtained via enzymatic hydrolysis using different sources of cellulose indicated that the Fenton pretreated RS gave the highest glucose concentration (26.36 mg/ml), followed by the α-cellulose (10.21 mg/ml) and raw RS (5.54 mg/ml). Fenton pretreatment is a simple and green approach to delignify the structure of RS for high recovery of glucose.

REFERENCES

[1] E. B. Belal, "Bioethanol production from rice straw residues," *Brazilian Journal of Microbiology*, vol. 44, no. 1, pp. 225–234, 2013.

[2] B. A. Goodman, "Utilization of waste straw and husks from rice production: A review," *Journal of Bioresources and Bioproducts*, vol. 5, no. 3, pp. 143–162, 2020.

[3] Y.Y. Gan, S.L. Zhou, X. Dai, H. Wu, Z.Y. Xiong, Y.H. Qin, J. Ma, L. Yang, Z.K. Wu, T.L. Wang, W.G. Wang, and C.W. Wang, "Effect of iron salt type and dosing mode on fenton-based pretreatment of rice straw for Enzymatic hydrolysis," *Bioresource Technology*, vol. 265, pp. 394–398, 2018.

[4] H.T. Yu, B.Y. Chen, B.Y. Li, M.C. Tseng, C.C. Han, and S.G. Shyu, "Efficient pretreatment of lignocellulosic biomass with high recovery of solid lignin and fermentable sugars using Fenton reaction in a mixed solvent," *Biotechnology for Biofuels*, vol. 11, no. 1, 2018.

[5] Y. H. Jung, H. K. Kim, H. M. Park, Y.C. Park, K. Park, J.H. Seo, and K. H. Kim, "Mimicking the Fenton reaction-induced wood decay by fungi for pretreatment of lignocellulose," *Bioresource Technology*, vol. 179, pp. 467–472, 2015.

[6] D. M. Kato, N. Elía, M. Flythe, and B. C. Lynn, "Pretreatment of lignocellulosic biomass using Fenton chemistry," *Bioresource Technology*, vol. 162, pp. 273–278, 2014.

[7] S. Wang, J. Sun, M. Chen, X. Hou, and Z. Gao, "Effect of Fenton pretreatment on enzymatic hydrolysis of poplar," *BioResources*, vol. 16, no. 1, pp. 1980–1987, 2021.