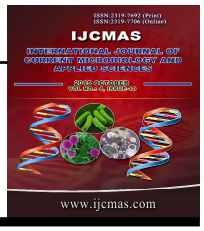
Int.J.Curr.Microbiol.App.Sci (2015) 4(10): 89-95

International Journal of Current Microbiology and Applied Sciences
ISSN: 2319-7706 **Volume 4 Number 10 (2015) pp. 89-95**
http://www.ijcmas.com



Original Research Article

The Effect of Sulfuric and Hydrochloric Acid on Cellulose Degradation from Pod Husk Cacao

Gatot S Hutomo*, Abdul Rahim and Syahraeni Kadir

Department of Food Science, Faculty of Agricultural, Tadulako University Jl, Sukarno-Hatta, KM 9 No 32 Palu, Central Sulawesi, 94118, Indonesia
**Corresponding author*

K e y w o r d s

Pod husk cacao, Cellulose, Degradation, Acid, Glucose

A B S T R A C T

Pod husk cacao content compounds such as pectin, lignin, hemicellulose, cellulose and others compound as polyphenols, caffein and theobromine. Delignification processing was used 12% sodium hydroxide, 6% sodium hypochloric and 6% sodium bisulfite. The cellulose powder by isolation from pod husk cacao would be used this research. The objectives of the research are about effectively cellulose degradation by an organic strong acid. The sulfuric acid and hydrochloric acid were used degradation for cellulose each in 1.0, 1.5, 2.0 and 2.5 M. Every two hours, glucose would be detected until 12 hours with 3 replication. The research showed cellulose degradation by sulfuric acid 1.0, 1.5, 2.0 and 2.5 M after 6 hours content 12.0, 16.7, 21.0 and 24.0% glucose respectively so that after 6 hours the glucose would be decreased. The cellulose degradation by hydrochloric acid in 1.0, 1.5 , 2.0 and 2.5 M after 8 hours content 10, 13, 15 and 19% glucose respectively so that stable after 8 hours. The result cellulose degradation by sulfuric acid would be high in glucose concentration compared with the hydrochloric acid. FT-IR spectra of origin cellulose were showed same FT-IR spectra from cellulose of pod husk cacao.

Introduction

Properties of cellulose base on fruits are difference than those of cellulose from cotton or wood. Normally commercially available cellulose has degree of polymerization about 983.40 units of anhydrous glucose and molecular weight about 159,408. Also it shows the isolated cellulose from pod husk cacao, the degree polymerization about are 390.40 and molekuler weight about 63.342 (Hutomo *et al.,* 2012). The short polymerization anhydrous glucoside will degrade more than the long chain by acid or enzyme. The cellulose can potentially make glucose or fructose syrup by acid or enzyme.

In Indonesia cacao beans produced was accounted about 800.000 tons in year 2012 that is amount equal to 8,000,000 ton pod husk cacao as by product containing 35% (db) cellulose (Sobamiwaand and Longe, 1994). Cellulose usually occurs in the cell

wall and is generally associates with many kinds of substances such as lignin, pectin and hemicellulose which make it difficult to find in pure form. Sodium hydroxide 12% would be separation the substances from cellulose. Cellulose isolation from pod husk cacao was used 12% sodium hydroxide and bleached 6% sodium hypochloride continued 6% sodium bisulfite (Hutomo *et al.*, 2012). Delignification used sodium hydroxide caused not degradation for anhydrous glucose in cellulose but made the lignin degradation. Bleaching by sodium hypochloride 6% would be oxidation the lignin to be polar so soluble in water and sodium bisulfite 6% would be reduction the lignin to be polar so soluble in water too. Lightness of cellulose would be showed about purity of cellulose form.

Cellulose potentially would be modified as carboxymethyl cellulose, hydroxy propyl cellulose, methyl cellulose and hydroxy propyl methyl cellulose (Olaru *et al.*, 1997; Hienze and Pfeiffer, 1999; Togrul and Arslan, 2004; Adinugraha *et al.*, 2005; Pushpamalar *et al.*, 2006; Suzana, 2009). The sulfuric acid and hydrochloric acid are strong acid but difference in effectively for cellulose degradation. The hydrochloric acid consist of one proton per mole so the sulfuric acid content two proton per mole. Cellulose degradation by acid is cheaper than by enzyme.

Material and Methods

Pod husk cacao (*Theobroma cacao* L) was obtained from Palolo District of Sigi, Central Sulawesi Province, Indonesia. Cellulose from pod husk cacao was isolated was used 12% Sodium hydroxide, 6% sodium hypochloric and 6% sodium bisulfite. Some compound are used sulfuric acid, hydrochloric acid, aqua bidest and acetonitrile.

Hydrolysis cellulose by acid

Obtained cellulose 5g in Erlenmeyer was added 200 ml sulfuric acid/hydrochlorid acid in 1.0, 1.5, 2.0, and 2.5 M so that heated at 100^{o}C. The glucose concentration was detected every 2 to 12 h with stirrer. The second step obtained cellulose 5g in Erlenmeyer was added 200 ml hydrochloric acid in 1.0, 1.5, 2.0, and 2.5 M so that heated at 100^{o}C. The glucose concentration was detected every 2 to 12 h by HPLC (High Performance Liquid Chromatography).

Glucose analysis

The High Performance Liquid Chromatography made in ICI, KORTEC type K25 (pump), KORTEC Gradient Controller type K45 and detector optical refractional type SODEX Ri-Se-61. Glucose concentration was detected by HPLC flow rate 1.00 ml/minute acetonitrile /water as 60 : 40 with type coloum C-18 in temperature 60□C (TC 1900 as temperature controller). Glucose standard was prepared in 10, 20, 30, 40, and 50 ppm, so that he standard and samples were injected 1 µl.

FTIR spectra analysis

FTIR spectra of cellulose were measured using KBr's method (Pushpamalar *et al.*, 2006). The dry starch sample was blended with KBr in a 1:4 ratio of starch/KBr. The mixture was pressed to obtain a pellet and introduced in the spectrometer (MIDAC, prospect 269, Costa Mesa, CA, USA). Each spectrum was analyzed in the range of resolution from 500 to 4000 cm^{-1}.

Result and Discussion

Cellulose degradation by sulfuric acid

Cellulose degradation by sulfuric acid with

various at concentration was showed at figure 1. The cellulose hydrolysis by sulfuric acid 1.0 M was showed at figure 1a. The research showed after 2 h degradation cellulose, the glucose concentration about 8.5% so that tend toward going up to 12% glucose at 6 h. The glucose concentration would be going down after 6.61 h, because the sulfuric acid should be oxidation to make degradation structure of glucose. Glucose would be broken 6 to 8 hours about 0.1146% per hour.

The cellulose hydrolysis by sulfuric acid 1.5 M was showed at figure 1b. The research showed after 2 h degradation cellulose, the glucose concentration about 11% so that tend toward going up to 16.7% glucose at 6 h. The glucose concentration would be going down after 7.01 h, because the sulfuric acid should be oxidation to make degradation structure of glucose too. Glucose would be broken 6 to 8 h about 0.4149% per hour. The cellulose degradation by sulfuric acid 2.0 M was showed at figure 1c. The research showed after 2 h degradation cellulose, the glucose concentration about 16% so that tend toward going up to 20.4% glucose at 6 h. The glucose concentration would be going down after 6.20 h, because the sulfuric acid should be oxidation to make degradation structure of glucose too. Glucose would be broken 6 to 8 h about 0.3978% per hour, whereas cellulose hydrolysis by sulfuric acid 2.5 M was showed at figure 1d. The research showed after 2 h degradation cellulose, the glucose concentration about 17% so that tend toward going up to 23% glucose at 6 h. The glucose concentration would be going down after 6.70 h, because the sulfuric acid should be oxidation to make degradation structure of glucose too. Glucose would be broken 6 to 8 h about 0.1515% per hour.

This result was in agreement with the finding of Idral *et al.* (2012) who reported to obtained a good hydrolysis time was 120 minutes because if the hydrolysis time too long then the glucose will be degraded and react further to form formic acid, resulting in decreased glucose levels. Previous researcher by Taherzadeh *et al.* (2008) also was obtained optimum hydrolysis time for 120 min in producing the highest glucose.

Cellulose hydrolysis by hydrochloric acid

Cellulose hydrolysis by hydrochloric acid with various at concentration was showed at figure 2. The cellulose hydrolysis by hydrochloric acid 1.0 M was showed at figure 2a. The research showed after 2 h degradation cellulose, the glucose concentration about 8% so that tend toward increase to 10% glucose at 8.97 h. The glucose concentration would be stable after 8 h, because the hydrochloric acid should not be oxidation of glucose. The cellulose hydrolysis by hydrochloric acid 1.5 M was showed at figure 2b. The research showed after 2 h degradation cellulose, the glucose concentration about 11% so that tend toward increase to 13% glucose at 8.69 h. The glucose concentration would be stable after 8 h, because the hydrochloric acid should not be oxidation of glucose. The Cellulose degradation by hydrochloric acid 2.0 M was showed at figure 2c. The research showed after 2 h degradation cellulose, the glucose concentration about 12.5% so that tend toward increase to 15% glucose at 8.91 h. The glucose concentration would be stable after 8 h, because the hydrochloric acid should not be oxidation of glucose.

The cellulose degradation by hydrochloric acid 2.5 Molar was showed at figure 2d. The research showed after 2 h degradation cellulose, the glucose concentration about 16.75% so that tend toward increase to 19% glucose at 8.63 h. The glucose concentration

would be going down after 8.63 h, because the hydrochloric acid in high concentration should be oxidation structure of glucose. Glucose would be broken 8.63 to 10 h about 0.0387% per hour. The research results (Tursiloadi *et al.*, 2009) using H_2SO_4 concentration of 0.5 to 2.5 M for hydrolysis of banana stem fiber at the temperature 85 and 100 °C for 270 min showed a linear or proportional relationship between the amount of H_2SO_4 concentration of glucose produced. Conversely, research by Fatmawati *et al.* (2008) showed the increase in the percentage of reducing sugar levels by an average of 4–6 mg/g or by 19.52% of H_2SO_4 concentration of 0.3% (a reducing sugar content 20.03 mg/g) to a concentration of 0.6% (reducing sugar content of 23.94 mg/g) and then amount was to 24.27% of the concentration of H_2SO_4 concentration of 0.9% (reducing sugar content of 29.75 mg/g) as rice straw cellulose hydrolysis products at 70, 85 and 100 °C for 1 hour.

Table.1 FT-IR spectra commercial and pod husk cacao of cellulose

Wavelenght (cm^{-1})		Group
Commercial cellulose	Cellulose of pod husk	
- 3410	- 3448	- OH Stretching
- 2893	- 2924	- CH stretching CH_2 & CH_3 groups
- 1373	- 1373	- OH in plane bonding
- 1056	- 1064	- C-O asymmetry bridge bonding
- 894	- 894	- 1,4-β glycoside

Figure.1 Glucose concentration from hydrolysis cellulose by sulfuric acid with concentration differences: (a) 1.0 M; (b) 1.5 M; (c) 2.0 M and (d) 2.5 M

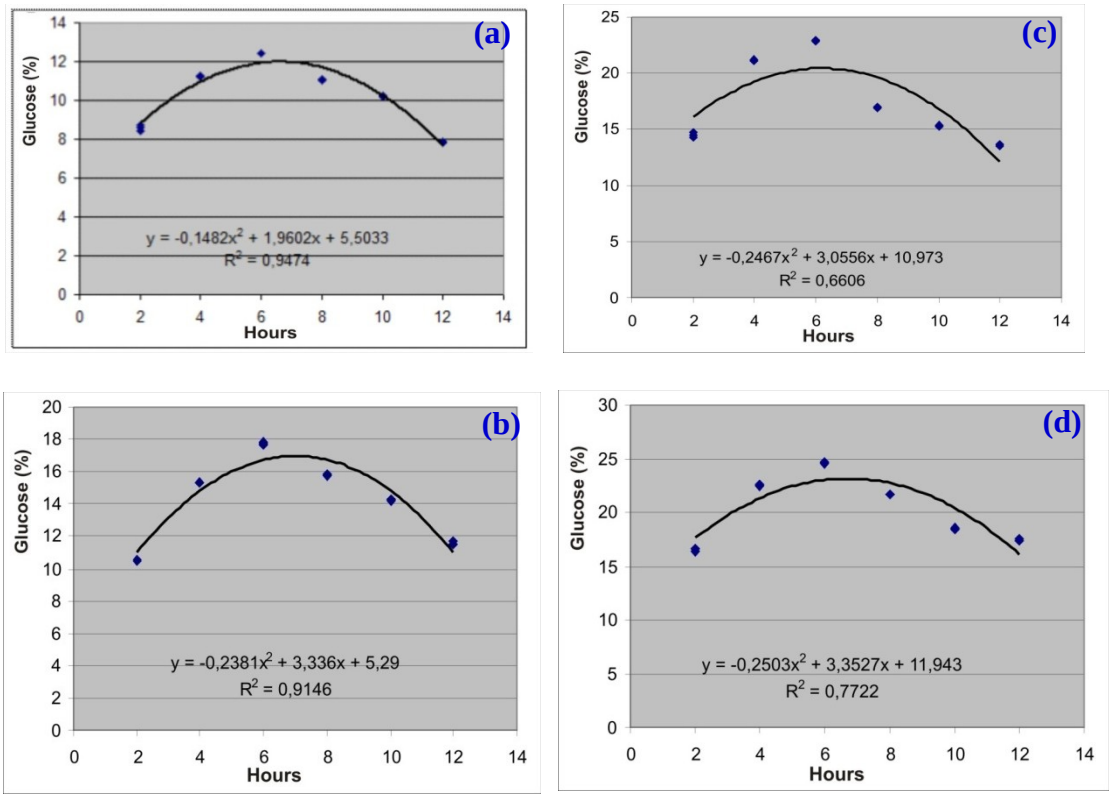


Figure.2 Glucose concentration from hydrolysis cellulose by hydrochloric acid with concentration differences: (a) 1.0 M; (b) 1.5 M; (c) 2.0 M and (d) 2.5 M

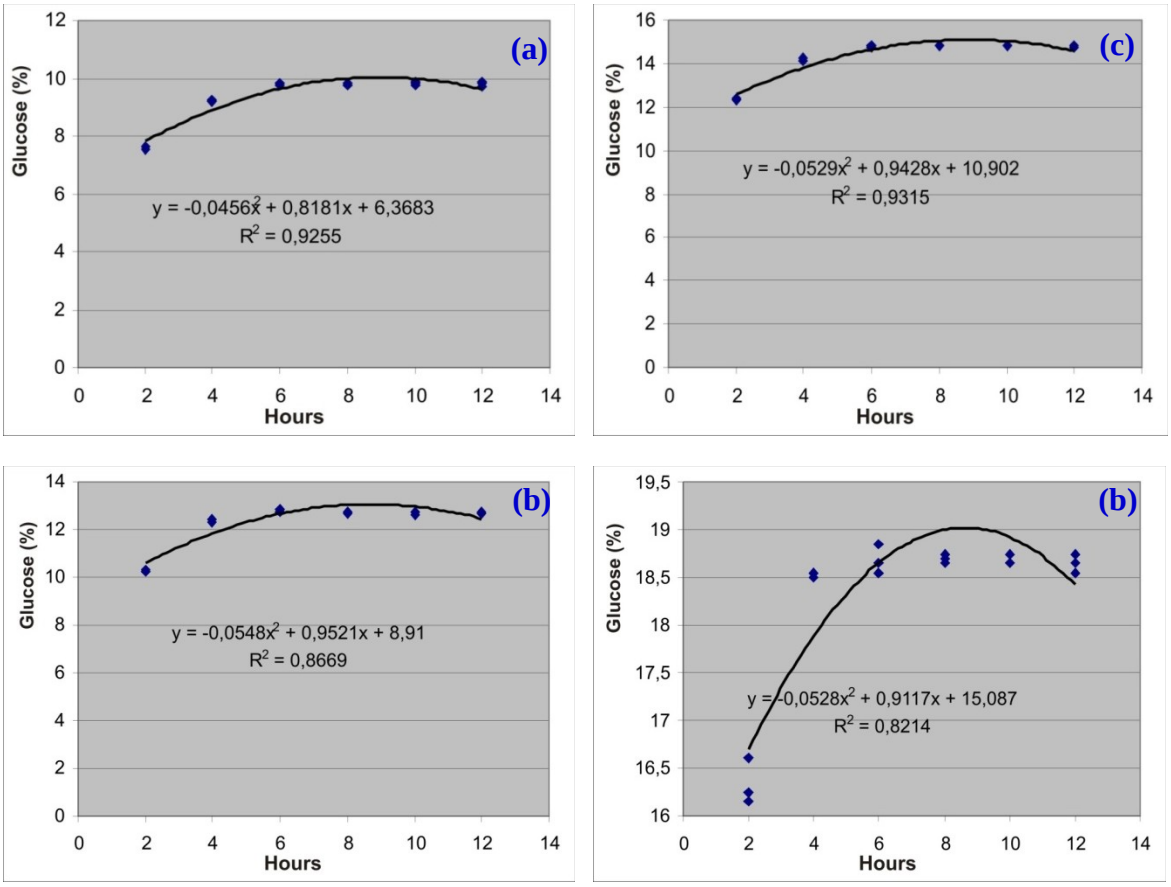
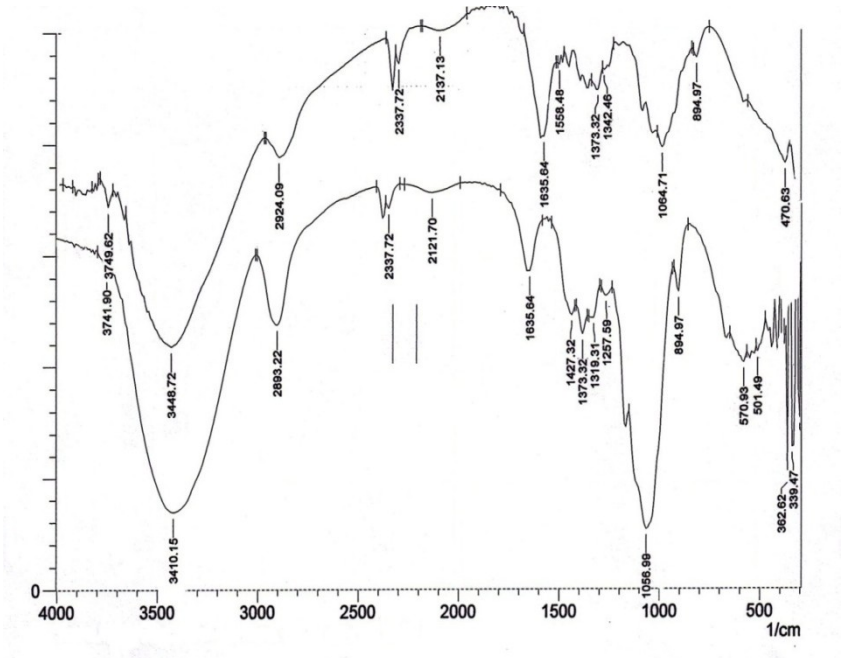


Fig.3 Infra-red spectra of commercial cellulose (A) and cellulose from pod husk cacao (B)



Infra-red spectra

Analysis of FT-IR spectra of origin cellulose was showed same FT-IR spectra from cellulose of pod husk cacao was showed at figure 3. Meenakhis *et al.* (2002) group –OH would be rise inplane deformation in wavelenght 3.448–3.410 cm^{-1} so that group -OH from cellulose at wavelenght 3448 cm^{-1}. Group C-O as stretching vibration was showed at wavelenght 1.064–1.056 cm^{-1} that it as peak wavelenght 1.064,31 cm^{-1} as group C-O in cellulose from Pod husk cacao. It was showed at wavelength 3.448 cm^{-1} as peak that it sign cellulose as stretching vibration and hydrogen linked intra-moleculer as -COH. Wavelenght 2924 –2893 cm^{-1} as some peaks of groups –CH dan $–CH_2$ from cellulose (Table 1). The linked of 1,4-β from cellulose would be rise at wavelenght 894 cm^{-1} that it is sign of cellulose (Viera *et al.,* 2007; Pecsok *et al.,* 1976).

The rising of some peak of group –OH, -CH, $-CH_2$ and 1,4-β linked with that showed as cellulose. The base lines of infra-red spectra of cellulose have the same peaks as stretching vibration and in plane deformation.

Hydrolysis of anhydrous glucose from cellulose by sulfuric acid is more high glucose concentration recovery than hydrochloric acid. Glucose would be broken by sulfuric acid in 1.0, 1.5, 2.0, and 2.5 M after 6 to 8 h about 0.1146, 0.4149, 0.3978, 0.1515% per hour, respectively. Hydrochloric acid less than 2.5 M for hydrolysis cellulose would be oxydation glucose to be broken.

Reference

Adinugraha, M.P., Marseno, D.W., Haryadi, 2005. Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (*Musa cavendishii* LAMBAERT). *J. Carbohydr. Poly.,* 62: 164–169.

Fatmawati, A., Soeseno, N., Chiptadi, N., Natalia, S. 2008. Rice straw hydrolysis using dilute sulfuric acid. *J. Chem. Eng.,* 3(1): 187–191.

Hienze, T., Pfeiffer, K. 1999. Studies on the sythesis and characterization of carboxymethyl cellulose. *J. Die Angenwandte Macromoleculare Chem.,* 266(4638): 37–45.

Hutomo, G.S., Djagal, W.M., Anggrhini, Supriyanto, 2012. Identification and characterization cellulose from pod Husk cacao (*Theobroma cacao* L). *J. Agritech.,* 32(3): 223–229.

Idral, D.D.M., Salim dan Mardiah, E. 2012. The making of bioethanol from sago waste by use of acid hydrolysis processing and Saccharomyces cereviceae. *J. Undana Chem.,* 1(1): 34–39.

Meenakshi, P., Noorjahan, S.E., Rajini, R., Venkatesvalu, U., Rose, C., Sastry, T.P. 2002. Mechanical and microstructure study on the modification of cellulose acetate (CA) film by blending with polystyren (PS). *Bull. Mater. Sci.,* 25(1): 25–29.

Olaru, N., Olaru, L., Stoleriu, A., Timpu, D. 1997. Carboxymethyl cellulose synthesis in organic media containing ethanol and or acetone. *J. Appl. Polymer Sci.,* 67: 481–486.

Pecsok, R.L., Shields, L.D., Caims, T., McWilliam, I.G. 1976. Modern methods of chemical analysis. Wiley, New York, NY.

Pushpamalar, V., Langford, S.J., Ahmad, M., Lim, Y.Y. 2006. Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *J. Carbohydr. Poly.,* 64: 312-318.

Sobamiwaand, O., Longe, O.G. 1994. Utilization of cocoa pod pericarp fractions in broiler chick diets. *J. Feed Sci. Technol.*, 47: 237–244.

Suzana, 2009. Synthesis and characterization of sodium carboxymethylcellulose from pineapple crown. Thesis of Post graduate, Food Science and Technology, Gadjah Mada University.

Taherzadeh, J., Muhammad, Karimi, K., 2008. Pretreatment of lignocellulosic waste to improve bioethanol dan biogas production. *Int. J. Mol. Sci.*, 9: 1621–1651.

Togrul, H., Arslan, N. 2004. Carboxymethylcellulose from sugar beet pulp cellulose as a hydrophylic polymer in coating of Mandarin. *J. Food Eng.*, 62: 271–279.

Tursiloadi, S., Sanjaya, K.G., Indrasti, N.S. 2009. Mathematical model of the process of hydrolysis of cellulose to glucose using banana stems liquid acid catalyst. *J. Technol. Indonesia Pert.*, 19(3): 164–169.

Viera, R.G.P., Filho, G.R., Assuncao, R.M.N., Meireles, C.S., Vieira, J.G., Oliveira, G.S. 2007. Synthesis and characterization of methylcellulose from sugar cane bagasse cellulose. *J. Carbohydr. Poly.*, 67: 182–189.