Cellulose acetate production from paddy rice straw and oil palm empty fruit bunch: trichloroacetate catalyst

R Maryana¹, M Anwar², S U Hasanah³, E Fitriana³, A Suwanto² and W A Rizal²

¹) Research Center for Chemistry, Indonesian Institute of Sciences, Tangerang Selatan, Banten, Indonesia
²) Research Division for Natural Product Technology, Indonesian Institute of Sciences, Gunungkidul, Yogyakarta, Indonesia
³) Department of Chemistry, Semarang State University, Gunungpati, Semarang, Jawa Tengah, Indonesia

*Corresponding author’s email: roni002@lipi.go.id; roni_yogya@yahoo.co.id

Abstract. The utilization of non-wood biomass for fuels and chemicals production is widely studied in recent years. This paper reported the application of trichloroacetate as catalyst in the production of cellulose acetate from paddy (Oriza sativa) rice straw and oil palm (Elaeis guineensis) empty fruit bunch (EFB). Firstly, pre-treatment by using H₂O in acidic condition was carried out prior to the soda pulping by using NaOH 10%, solid to liquid ratio 1:7. The pre-treatment and pulping aim to separate cellulose from lignin and hemicellulose. Furthermore, in order to purify the cellulose, bleaching was applied to the pulps by using NaClO₂ 0.5% and H₂O₂ 10%. Finally, the paddy rice straw pulp and oil palm EFB pulp were subjected to the acetylation by using acetic anhydride as acetylating agent in CH₃COOH condition with catalyst CCl₃COOH and H₂SO₄. The analysis results by using Fourier-transform infrared spectroscopy showed that C=O stretching from cellulose acetate at around 1730 cm⁻¹. Furthermore, the morphological surface and crystallinity of the raw materials and products was analysed by using scanning electron microscopy and X-ray diffraction, respectively. The acetylated cellulose diameter and cristallinity decreased after the acetylation reaction.

1. Introduction

Besides known as the largest crude palm oil production (CPO) in the world, Indonesia is also known as agricultural country. Paddy rice is planted widely and become the national primary food. Statistics Indonesia reported that the plantation area for oil palm reached 14.3 million hectares in 2018 and produced 40.5 million tons [1]. Meanwhile paddy rice was planted in 10.9 million ha and produced about 56.5 million tons [1]. Both commodity resulted biomass waste during the processing and the biomass waste contains mostly cellulose, lignin and hemicellulose. Cellulose is very important chemical substance. This organic compound can be utilized as raw material for many derivative products. Cellulose is a polysaccharide consisting of a linear chain of D-glucose with several hundred to many thousands units that linked together by β linked. It was reported that biomass cellulose can be utilized for producing bioethanol and dissolving pulp [2]. Furthermore, cellulose can be reacted to produce chemicals. One of the important cellulose derivatives is cellulose acetate. Cellulose acetate is generally produced from wood fibres cellulose by acetylation reaction by using acetic anhydride with sulfuric acid catalyst. During the acetylation, the hydrogen in the hydroxyl (OH) groups of glucose
unit is replaced by acetyl groups (CH$_3$-CO). The hydroxyl (OH) groups in the glucose is presented in Figure 1.

![Figure 1. Hydroxyl (OH) groups in the glucose unit as cellulose monomer](image)

Cellulose acetate has been known has wide application in the chemical industry such as raw materials for textile, food packaging, film coating, filtration and separation etc. [3-8]. Therefore, this study aims to utilize biomass waste from oil palm empty fruit bunch (EFB) and paddy rice straw (RS) for cellulose acetate production as alternative raw materials. Novelty of this study is the application trichloroacetate catalyst in the acetylation of oil palm EFB cellulose and paddy RS cellulose by using acetic anhydride as cellulating agent. Generally the production of cellulose acetate was carried out by using conventional method or recent synthetic methods for esterification such as ionic liquid [9] and iodine catalyst [10].

2. Materials and methods

2.1. Materials

Oil palm EFB was collected from PT Ladang Sawit Mas, Kalimantan Barat and paddy rice straw was collected from rice field in Bantul region, Yogyakarta. Chemicals used in this study are acetic anhydride from ajax chemicals, acetic acid (glacial) 100% from Merck, trichloroacetic acid from Merck and sulfuric acid 95-97% from Merck.

2.2. Methods

2.2.1 Delignification

Each 25 gram of oil palm EFB and paddy RS was prepared in the stainless steel reactor 76 mm in diameter and 255 mm in height. Distilled water was then added with solid to liquid ratio 1:12, followed by addition H$_2$SO$_4$ 0.1% w/v. The reactors were heated at 150 °C for 2 hours. After the process, solid residue was filtered and subjective to the delignification process. Delignification was carried out in the same reactor by adding sodium hydroxide 10% with solid to liquid ratio 1:7. The reaction condition was 150 °C for 2 hours. After the process, solid residue rich in cellulose was filtrated from liquid phase or black liquor which is rich in lignin content.

2.2.2 Bleaching

As much as 25 g each pulps of oil palm EFB and paddy RS, was subjected in to erlenmeyer flask and NaClO$_2$ 0.5% was added with solid to liquid ratio 1:12. Subsequently, 0.5 ml CH$_3$COOH p.a was added, the solution heated at 80 °C for 1.5h. After first bleaching, solid and liquid phase were filtrated and the solid residue was washed until pH about 7. The second bleaching was carried out by adding H$_2$O$_2$ 10% after the first bleaching with solid to liquid ratio 1:12. The conditions for second bleaching were 70 °C for 5 h. After heating and then cooling, solid residue was filtrated and washed until neutral pH.
2.2.3 Acetylation
Each 5 g of oil palm EFB and paddy RS cellulose was prepared in the 250 ml erlenmeyer flask. As much 90 ml acetic acid glacial and 0.22 g trichloroacetic acid were added to the cellulose and mixed at 40°C overnight. Then, 0.125 ml H$_2$SO$_4$ and 25 ml acetic anhydride were added to the erlenmeyer and the solution was mixed for 30 min in room temperature and was aging for 48h. Furthermore, 0.125 g CH$_3$COONa in 10 ml acetic acid glacial was added and stirred for 15 min at room temperature. Finally, 100 ml distilled water was added and mixed for 15 min. The solid residue, the cellulose acetate, was then filtrated and be washed by distilled water.

2.3 Material characterization
Chemical characterization of such as cellulose, hemicelluloses and lignin content was carried out by using Chesson-Datta method. Fourier Transmission Infrared Spectroscopy IR Prestige 21 – Shimadzu was used for study functional group of cellulose and cellulose acetate. Meanwhile, Scanning Electron Microscope (SEM) SU-3500 from Hitachi, Tokyo, Japan was used for surface characterization and X-ray diffraction was used crystallinity samples.

3. Results and discussions
Delignification of oil palm EFB and paddy RS was carried out in the stainless steel reactor by using sodium hydroxide 10%. Before alkaline delignification, pre-treatment with distilled water in acidic condition was performed in order to remove hemicellulose. The chemical composition of raw material and pulp after delignification is presented in Table 1. Based on the Table 1 cellulose content of oil palm EFB increased by 87% after delignification. Meanwhile hemicellulose and lignin content decreased 53 and 57%, respectively. Regarding paddy RS, cellulose content increased 139%, hemicellulose and lignin decreased 75 and 72%. It is showed that paddy RS easier to be delignified than oil palm EFB. The rest of chemical compound are extractives and organic acids.

| Sample                  | Oil palm EFB | Paddy rice straw |
|-------------------------|--------------|------------------|
|                         | Cellulose (%)| Hemicellulose (%)| Lignin (%) | Cellulose (%)| Hemicellulose (%)| Lignin (%) |
| Raw material            | 38.70        | 17.21            | 28.06      | 31.89        | 21.77          | 11.53      |
| Pulp after delignification | 72.38        | 8.11             | 12.09      | 76.10        | 5.4            | 3.2        |

After delignification, pulps of oil palm EFB and paddy RS were subjected into two steps bleaching processes. In the first bleaching, sodium chlorite was used. The advantages of sodium chlorite are high brightness degree and minimum environmental impact, because the waste water has negligible halogenated organic compound (AOX). In the second bleaching, hydrogen peroxide was used. Hydrogen peroxide has known as a total chlorine free bleaching agent and has both oxidizing and reducing properties depend on its pH condition. In the paper industry, H$_2$O$_2$ has applied widely for bleaching agent because it can improve paper quality, increase yield percentage and environmental friendly.

Regarding cellulose acetate production, the heterogeneous acetylation was carried out using bleached pulp oil palm EFB and paddy RS. Acetic anhydride was used as acetylating agent and trichloroacetic acid and sulfuric acid as catalyst in the present of acetic acid. The advantages of trichloroacetic acid could be similar with the advantages of trifluoroacetic acid catalyst during acetylation reaction. Morgan reported that trifluoroacetic acid would minimize co-products formed during acetylation. In the case using just sulfuric acid as catalyst, the co-products can bound acid sulfate groups and inhibit the reaction [11]. During the acetylation reaction, some polar hydroxyl
groups of cellulose from oil palm EFB and paddy RS were substituted by acetyl groups. The properties of the derivative cellulose might be changed and altering its solubility properties in the organic solvent. Besides oil palm EFB and paddy RS, the acetylation reaction was also performed for three kinds of the mixed samples. The samples name for oil palm EFB dan paddy RS were A, for ratio 1:1; B for ratio 1:3 and C for ratio 3:1.

Meanwhile, degree of substitution (DS) of the cellulose acetate resulted from the reactions have been analysed and is presented in the table 2.

| Sample name       | Degree of Substitution (DS) |
|-------------------|-----------------------------|
| Oil palm EFB      | 0.84                        |
| Paddy RS          | 0.21                        |
| A - EFB:RS (1:1)  | 0.75                        |
| B – EFB : RS (1:3)| 0.71                        |
| C – EFB:RS (3:1)  | 0.83                        |

It is showed that all the DS values samples were lower than 1. Based on this result, the acetylation reaction was not yet completed. Only one hydroxyl group successfully be replaced by acetyl group. The DS value if all the hydroxyl group can be replaced by acetyl group will be 3. Therefore, the optimization in the reaction condition such as temperature and time need to be determined to increase DS value to 2 and 3. Regarding DS value, oil palm EFB showed the highest DS, 0.84 compared to others. Moreover, for sample C, which is ratio for EFB and RS 3:1, the DS value was also high, 0.83. It can be concluded that DS value for oil palm EFB was higher than those of paddy RS.

![Comparison of IR spectra of commercial cellulose, acetylated cellulose of oil palm EFB, paddy RS and mixed samples](image)

**Figure 2.** Comparison of IR spectra of commercial cellulose, acetylated cellulose of oil palm EFB, paddy RS and mixed samples

IR spectra of acetylated cellulose of samples were compared to those of commercial cellulose and commercial cellulose acetate. The spectra at 1728-1743 cm⁻¹, is an indication of C=O stretching of carbonyl ester band [12]. Figure 2 showed no peak appeared at around 1730 cm⁻¹ for cellulose spectra, because cellulose has no C=O bonding from acetyl groups. Meanwhile for cellulose acetate spectra,
there was strong peak at this point. The C=O stretching is one of indicators for the present of cellulose acetate. Based on figure 2, it can be seen that for acetylated cellulose from oil palm EFB, paddy RS and mixed sample A to C showed peak but the intensity was not very strong. These results correlated with the low DS value for all samples (< 1). Meanwhile, in the case of commercial cellulose, there was strong intensity at 1369 cm\(^{-1}\) that indicated C-H bending vibration. Moreover, the intensity at around 1220 cm\(^{-1}\) increased in the acetylated cellulose compared to those of cellulose. This intensity belonged to the stretching vibration of C-O.

Morphologies and surface structure of cellulose acetate were studied by using Scanning Electron Microscopy (SEM) and is presented in figure 3.

![SEM micrograph for acetylated cellulose paddy RS (a), oil palm EFB (b), sample A (c), sample B (d), sample C (e), commercial cellulose (f) and commercial cellulose acetate (g)](image)

**Figure 3.** SEM micrograph for acetylated cellulose paddy RS (a), oil palm EFB (b), sample A (c), sample B (d), sample C (e), commercial cellulose (f) and commercial cellulose acetate (g)

The diameter and length of acetylated cellulose for all samples generally decreased compared to those of commercial cellulose. Crystallinity of the acetylated cellulose of samples was determined by using X-ray diffraction and is presented in figure 4.
Figure 4. XRD spectra for commercial cellulose (a), and acetylated cellulose paddy RS (b), oil palm EFB (c), sample A (d), sample B (e) and sample C (f)

The diffractograms of the acetylated cellulose were compared to those of cellulose. The high intensity peak showed the crystallinity structure of the materials. Based on figure 4, high intensity crystalline peak at $2\theta=22^\circ$ and an amorphous peak with intensity $2\theta=18^\circ$. Compare to the commercial cellulose (figure 4a), after acetylation process, the crystallinity decreased about 50%. However, crystallinity of acetylated cellulose was still high that indication of there was still cellulose in the samples.

4. Conclusion
The isolation of cellulose from oil palm EFB and paddy RS was carried out by alkaline pretreatment followed by two steps bleaching process by using sodium chlorite and hydrogen peroxide. Cellulose was successfully esterified by using acetic anhydride as acetylation agent and in $\text{CH}_3\text{COOH}$ condition with catalyst $\text{CCl}_3\text{COOH}$ and $\text{H}_2\text{SO}_4$. The acetylated cellulose of all samples showed peak intensity by FTIR at around 1730cm$^{-1}$ as indication of the presence of C=O bonding. The acetylation process decreased crystallinity and length of the fibre of acetylated cellulose.

References
[1] Statistics Indonesia. 2018. *Dynamic table of Plantation Area by Province* 09 04 838
[2] Maryana R, Nakagawa-Izumi A, Kajiyama M, Ohi H.. 2017 *J. of Fiber Science and Tech*. 73 8 182-191
[3] Gemili S, Yemenicioğlu A, Altinkaya S 2007 *J. of Food Engineering* 90 4 453-462
[4] Kumar VK, Kumar KK, Kishore PV, Sushma S 2015 *Res. J. Pharm*. 6 4 249-255
[5] Reddy N and Yang Y. 2005 *Trends in Biotechnology* 23 1 22-27
[6] Warth H, Mülhaupt R , Schätzle J 1997 *J Appl Polym Sci* 64 213–242
[7] Duarte A.P., M. T. Cidade, J. C. Bordado. 2006 *J Appl Polym Sci* 100 40 52–4058.
[8] Najafi, M, Sadeghi M, Bolverdi A, Chenar M, Pakizeh M. 2018. *Adv Polym Technol*. 37 2043–2052.
[9] Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., & Guo, M. 2004. *Biomacromolecules* 5 266–268.
[10] H.N. Chenga, Michael K. Dowda, G.W. Selling, Atanu Biswas 2010 *Carbohydrate Polymers* **80** 449–452

[11] Morgan, PW. 1951. *Industrial and Engineering Chemistry* **43** 11 2575-2577

[12] Das AM, Ali AA, Hazarika MP. 2014. *Carbohydrate Polymers* **112** 342–349