



Comparison Study of Various Cellulose Acetylation Methods from its IR Spectra and Morphological Pattern of Cellulose Acetate as a Biomass Valorisation

Roni Maryana*†, Muslih Anwar**, Andri Suwanto**, Siti Uswatun Hasanah*** and Eka Fitriana****

*Research Center for Chemistry, Indonesian Institute of Sciences, Building 452, Kawasan PUSPIPTEK, Serpong Tangerang Selatan, Banten, Indonesia

**Research Division for Natural Products Technology, Indonesian Institute of Sciences, Jl. Yogya Wonosari, Gading, Playen, Gunungkidul, Yogyakarta, Indonesia

***Department of Chemistry, Semarang State University, Gedung D6 Lantai 2, Kampus FMIPA UNNES, Sekaran, Gunungpati, Semarang, Jawa Tengah, Indonesia

†Corresponding author: Roni Maryana; roni_yogya@yahoo.co.id

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 18-07-2019

Accepted: 05-10-2019

Key Words:

Cellulose acetate;
Cellulose; Catalyst;
Trichloroacetate;
Acetylation

ABSTRACT

Recently substitution of fossil fuel-based polymer by natural polymer sources has been studied. Cellulose acetate that can be produced from the cellulose of biomass waste is an environmentally friendly and important polymer with many applications. This study was undertaken to determine the most suitable and effective method in the cellulose acetate (CA) production. Moreover, the role of catalyst and usefulness of trichloroacetate and I_2 catalyst has been studied. As many as 12 methods of acetylation for CA synthesis has been carried out, and the results have been compared. The peak height ratio of infrared (IR) spectra of acetyl groups was studied to determine the formation of CA. The result showed that the activation step resulted in higher IR spectra peak than the direct synthesis method. An important result of this study was shown when trichloroacetate catalyst combined with H_2SO_4 resulted in significantly higher IR spectra than the conventional method. Interestingly, I_2 catalyst resulted in better IR spectra peak than H_2SO_4 did, even the activation step was not performed. It showed that the addition of trichloroacetate and I_2 in the CA synthesis with acetic anhydride as an acetylating agent was better than conventional CA acetylation method. Furthermore, I_2 catalyst showed the best result among other methods and will be the promising pathway to produce CA. Scanning electron microscopy (SEM) analysis showed that the diameter of cellulose fibre was decreased and fracture surface occurred after the synthesis reaction.

INTRODUCTION

Indonesia, as well as other regions near the equator, generally have abundant biomass sources. Palm oil is one of the widely planted plants in Indonesia. Based on the statistics of Indonesia in 2018, the plantation area for oil palm is 14.3 million ha (Statistics Indonesia 2018). During processing, biomass waste such as oil palm empty fruit bunch, oil palm trunk and kernel were produced. Other potential agricultural waste biomass such as sugarcane bagasse, rice straw, forest and wood residue is also available in huge quantity. Cellulose is a major compound of biomass, besides lignin and hemicellulose. Biomass utilization for producing fuels such as bioethanol and dissolving pulp from cellulose; and chemical products such as xylitol from hemicellulose, sodium lignosulphonate and vanillin from derivatization of lignin has been reported (Judiawan 2019, Messaoudi 2019, Maryana 2017, Pramudono 2018). Another study reported the production of ethanol, lignin, and carbon source for fungal culture from

lignocellulosic materials (Smichi 2018). Enzyme production such as cellulase, xylanase, and ligninolytic that utilized agricultural biomass from biomass waste has also been studied (Namasivayam 2014, Rajwar 2016).

The cellulose-derivatives study has also gained high attention in the recent year since the lignocellulosic biomass could be a raw material for a valuable chemical and widely apply in industry. Cellulose acetate, the most important esters of cellulose, has wide application such as thermoplastics, textile industry, food packaging, film coating, reverse osmosis, and gas separation (Warth 1997, Reddy & Yang 2005, Gemili 2008, Kumar 2015, Duarte 2006, Najafi 2018).

Introducing acetyl functional group to the cellulose has been known as efficient derivatization of cellulose, one of them is cellulose acetate production. Many methods have been developed to produce cellulose acetate. In general, cellulose acetate is produced from the reaction of cellulose with acetic anhydride in acetic acid condition by using H_2SO_4 as

catalyst (Hummel 2004). Several studies have been reported to modify this conventional method. It has reported the addition of NaHSO_4 as a catalyst to reduce H_2SO_4 amount and to make the temperature of acetylation reaction becoming lower (Djuned 2014). Meanwhile, a study by using strong organo-halogen acid, trifluoroacetic acid, as a catalyst has also been studied (Morgan 1951). Morgan reported that trifluoroacetic acid catalyst would prevent derivative products formed during the acetylation of cellulose that could bound acid sulfate groups if the sulfuric acid catalyst is used. Another study used I_2 as a catalyst in a heterogeneous medium in the presence of acetic anhydride. Iodine catalyst mechanism reaction was proposed and is presented in Fig. 1 (Das 2014). Iodine is currently studied extensively as a catalyst because of its economic factor, convenience and environmentally friendly. Meanwhile, trichloroacetate, the catalyst in this study, has been known as powerful organic acid with $\text{pKa}1$ 0.66 compared with acetic acid $\text{pKa}1$ 4.756 and similar to trifluoroacetate $\text{pKa}1$ 0.52 (Lide 2004). Morgan (1951) reported that in the case of trifluoroacetate, the cellulose esters prepared by using this catalyst, will not need special washing because of the complete removal of catalyst. Moreover, it will not combine with alcohol in the presence of other carboxylic acids (Morgan 1951). Meanwhile, iodine has been known to react to form a complex with amylose and cellulose (Wang 1999). Therefore, this complex reaction could improve solubility of cellulose in the acetylation process. The previous study reported that acetylation of alcohol by acetic anhydride was promoted by iodine (Phukan 2004).

This study was carried out to determine the most suitable and effective method in the cellulose acetate (CA) synthesis. Moreover, the role of catalyst and usefulness of trichloroacetate and I_2 catalyst will be studied and be compared to the catalyst that is used in the conventional method synthesis. We focused on the role of catalyst and usefulness of trichloroacetate and I_2 in the cellulose acetate (CA) synthesis. The effective methods among available and modified methods

will be important for cellulose acetate production from biomass. Furthermore, we reported the new several catalyst combinations such as $\text{H}_2\text{SO}_4/\text{CCl}_3\text{COOH}/\text{NaHSO}_4$ and $\text{H}_2\text{SO}_4/\text{CCl}_3\text{COOH}$ in the cellulose esterification.

MATERIALS AND METHODS

Materials

The commercial pure cellulose C6228 fibres were obtained from Merck and cellulose acetate with average Mn 30,000 by GPC was obtained from Aldrich chemistry. The reagents used for the acetylation were acetic anhydride from ajax chemicals; Acetic acid (glacial) 100% from Merck; Trichloroacetic acid from Merck; Iodine from Merck; Sulfuric acid 95-97% from Merck; Sodium thiosulfate pentahydrate from Merck and Sodium hydrogen sulfate monohydrate from Merck.

Methods

The cellulose acetates were prepared by using twelve different methods. The experimental design with 12 methods is presented in Table 1, and the methods from 1 to 12 were named A to L, respectively. The acetylation procedures were categorized as three steps, activation; acetylation; and hydration. Method A and B (conventional method with activation step); method C (conventional method without activation); method D, E, F, G (using I_2 catalyst); method H (using H_2SO_4 and NaHSO_4 catalyst); J, K, L (catalyst combination including trichloroacetate).

Material characterization: Functional groups of cellulose and cellulose acetate were studied by using Fourier Transmission Infrared Spectroscopy. The samples were blended with KBr and followed by compressing this mixture in the sample disc and analysed with the transmission wavenumber range 4000 to 400 cm^{-1} . Meanwhile, the surfaces of the samples were analysed by using Scanning Electron Microscope (SEM), with SE 5 kV 2000x to 2500x magnification.

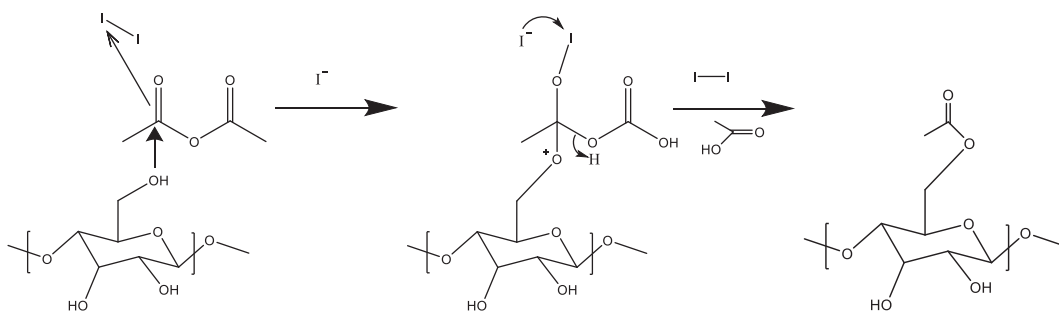


Fig. 1: Mechanism of cellulose acetate production by using iodine catalyst.

RESULTS AND DISCUSSION

Currently, the utilization of infrared spectroscopy is considered as one of the most important techniques. It was well known that infrared techniques provide fast, low-cost analysis, besides the non-destructive method with promising results (Xu 2013). Chemically, hundreds of glucose molecules linked by a glycosidic bond to form cellulose (Zugenmaier 2001). Meanwhile, FTIR is an efficient method to study hydrogen-bonding in the crystalline and amorphous structure of cellulose (Kondo 1996). Therefore, IR spectroscopy is a suitable method for studying CA characteristics, especially to observe the ester and hydroxyl group absorption. These functional groups are referred to CA formation in the synthesis of CA from cellulose.

The cellulose acetylation methods that were carried out in this study can be divided into three major steps (i) activation; (ii) acetylation; and (iii) hydration. Fig. 2 shows the IR spectra of twelve acetylated samples that were further compared to the IR spectra of cellulose and cellulose acetate. The peak height $1728\text{--}1743\text{ cm}^{-1}$, an indication of $\text{C}=\text{O}$ stretching of carbonyl ester band, as compared to the adsorbed water band at $1635\text{--}1651\text{ cm}^{-1}$ (Das 2014) and the height ratio was determined based on this comparison.

It was observed from Fig. 2 that the major change of stretching band of acetylated samples was at $1728\text{--}1743\text{ cm}^{-1}$ and $1635\text{--}1651\text{ cm}^{-1}$. Cellulose fibre has no peak at $1728\text{--}1743\text{ cm}^{-1}$ because it has no carbonyl ester group. Meanwhile, pure cellulose acetate showed the highest peak among acetylated cellulose samples. Sample methods A and B were previously treated with CH_3COOH and H_2SO_4 at 40°C for 3h as activation step before acetylation step. Activation step aims to open hydrogen bond in the hydroxyl functional group to make the acetylation process with acetic anhydride easier. The difference in sample method A and B was in the acetylation step, ratio $(\text{CH}_3\text{CO})_2\text{O} : \text{H}_2\text{SO}_4$ was 2 and 10 for sample A and B, respectively. Meanwhile, sample code C was acetylated without activation step. The results in Table 2 showed that the IR peak ratio for sample A (0.51) is higher than the peak of sample B (0.22). This phenomenon can be explained by the quantity of H_2SO_4 catalyst, for sample method A, sulfuric acid was 2.5 mL, and this was more than for the sample B (1 mL). This result supports many of the previous studies that the catalyst is important for the conventional acetylation method. In the case of method B, the sulfuric acid was not enough to catalyse the reaction. Regarding method C, the sample showed no peak at all. In this case, it has no peak because besides no activation step, the

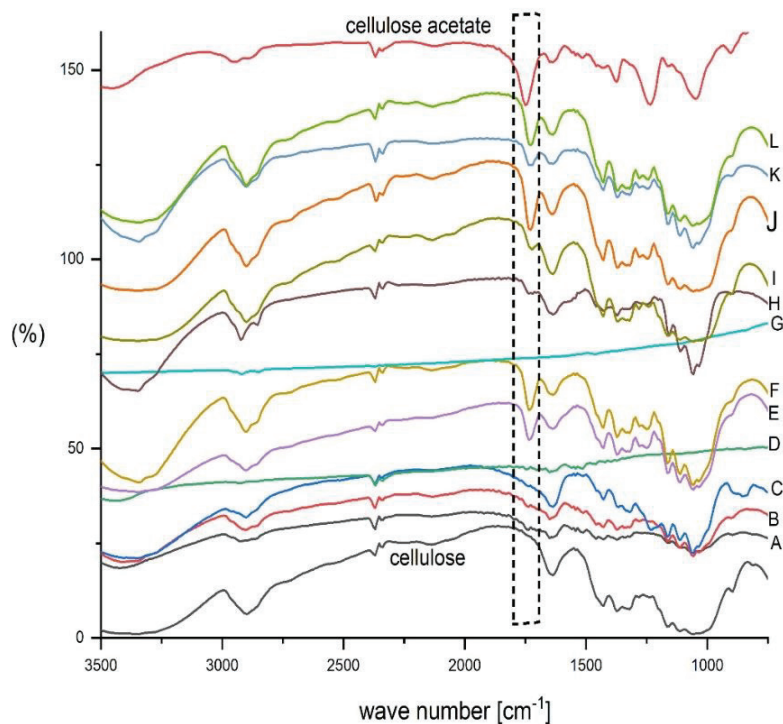


Fig. 2: Comparison of IR spectra of cellulose, acetylated cellulose with sample code A-L and cellulose acetate.

Table 1: Experimental design of twelve methods of cellulose acetate synthesis.

Sample code	Sample weight (g)	Activation	Acetylation	Hydration/further treatment
A	2	CH ₃ COOH 3M, 50mL H ₂ SO ₄ 98%, 2.5mL	reflux 40°C, 3h (CH ₃ CO) ₂ O 5mL H ₂ SO ₄ 98% 2.5mL	reflux 40°C, 8h
B	2	CH ₃ COOH 3M, 50mL H ₂ SO ₄ 98%, 2.5mL	reflux 40°C, 3h (CH ₃ CO) ₂ O 10mL H ₂ SO ₄ 98% 1mL (CH ₃ CO) ₂ O 2.9mL	reflux 40°C, 8h CH ₃ COOH 0.4mL
C	1		CH ₃ COOH 2.9mL H ₂ SO ₄ 98% 0.29mL	7°C, 1h H ₂ SO ₄ 98% 0.4mL Aging 15h
D	1		(CH ₃ CO) ₂ O 50mL, I ₂ 1.5g	reflux 80°C, 5h Filter and wash Residue is dissolved Filtrate is evaporated Na ₂ S ₂ O ₃ 5 H ₂ O 25 mL C ₂ H ₅ OH 150 mL room temp. stirrer 1 h ethanol 75% and aquadest CH ₂ Cl ₂
E, F, G	1		(CH ₃ CO) ₂ O 50mL, I ₂ 1.5g	reflux 120°C, 5h Filter and wash Residue is dissolved Filtrate, Residue (E) Residue is bleached (F) Filtrate is evaporated (G) CH ₂ Cl ₂
H, I	5	CH ₃ COOH 90mL	(CH ₃ CO) ₂ O 25mL H ₂ SO ₄ 98% 0.125mL NaHSO ₄ 0.19g	stirrer 30 min. at room temp. Aging for 3h Aquadest 1L to form solid phase Filtrate was evaporated (H) Residue (I) stirrer 15 min. at room temp.
J, K, L	5	CH ₃ COOH 90mL H ₂ SO ₄ 98% 0.125mL CCl ₃ COOH 0.22g (J) CH ₃ COOH 90mL H ₂ SO ₄ 98% 0.125mL CCl ₃ COOH 0.22g NaHSO ₄ 0.19g (K) CH ₃ COOH 90mL H ₂ SO ₄ 98% 0.125mL NaHSO ₄ 0.19g (L)	stirrer 1h at room temperature (CH ₃ CO) ₂ O 20mL	stirrer 30 min. at 40°C; Aging for 4h, 40°C CH ₃ COONa 0.125g in 10 mL CH ₃ COOH Aquadest 1L to form solid phase Filtrate was evaporated Residue stirrer 15 min. at 40°C

acetylation condition, temperature and time were decreased to 7°C and 1 h compared to 40°C for 8 h in the method A and B. The result confirmed the importance of activation step and suitable acetylation condition.

Samples with method D, E, F, G were acetylated without activation step. However, the iodine catalyst was used in the acetylation reaction. Sample method D was acetylated at 80°C for 5 h. The difference in the sample method E, F, G is the acetylation temperature; for these three samples, acetylation conditions were at 120°C for 5 h. From Fig. 2 and Table 2, it can be seen that the peak height ratio for method D at 80°C (0.49) was lower than those of method E and F at 120°C (1.75 and 2.01 for sample E and F). Meanwhile, sample G has no peak because this was the side product of method E and F. Regarding differences, E and F methods were bleached by H₂O₂ 10%. Method E was the unbleached sample, and F was the bleached one. In case of the sample with method G, after adding sodium thiosulphate and transferring the mixture to the beaker containing ethanol, the product was filtered and the residue becoming sample E and filtrate was sample G. It can be observed that there was no cellulose acetate in the filtrate.

Method H and I were similar to the conventional method. However, the activation step was carried out by using acetic acid and mixing for one hour in the room temperature. Additionally, in the acetylation step, sodium bisulphate, together with sulfuric acid was used as a catalyst. It was observed that both showed adsorption peak around 1730 cm⁻¹, the peak height ratio was 0.27 for H and 0.40 for I.

These results were lower than those of conventional method with activation step, A and B. The activation step for H and I was only by adding CH₃COOH. Meanwhile, in the case of A and B, the CH₃COOH and H₂SO₄ were added and mixed at 40°C for 3 hours. It seems that the activation condition gave significant influence, even sodium bisulphate was added in the acetylation step.

Method J, K, L were modified method of H and I. For the J method, the new combination of catalyst CH₃COOH, H₂SO₄, and CCl₃COOH were applied. Meanwhile, for the K method, also the new catalyst combination CH₃COOH, H₂SO₄, CCl₃COOH, and NaHSO₄ was studied. Furthermore, for sample code L, a new combination of catalyst CH₃COOH, H₂SO₄, and NaHSO₄ in the activation step was applied. It was observed that peak heights of J, K, L method were much better than those of H and I. For J method, the peak ratio was 1.94 and the better than those of K method (1.43) and L method (1.74). We can study the effect CCl₃COOH catalyst by comparing method J and method L. It was observed that method by using trichloroacetate was the best among all conventional methods. We can conclude that CCl₃COOH as powerful organic acid showing a significant role in the cellulose acetate formation.

However, interestingly, we found that iodine catalyst, method F, showed better peak height ratio than the conventional method by adding trichloroacetate, J method. Therefore, we confirm that method with using iodine catalyst is the best method and a promising catalyst in the cellulose acetate production.

Table 2: Peak height ratio of the carbonyl functional group to the adsorbed water band.

No	Method name	Peak Height (Δ %T)		Ratio 1735/1651
		1728-1743 cm ⁻¹	1635 -1651 cm ⁻¹	
1	A	1.41	2.79	0.51
2	B	0.87	3.98	0.22
3	C	0.00	7.16	0.00
4	D	0.60	1.22	0.49
5	E	7.90	4.52	1.75
6	F	9.90	4.78	2.07
7	G	-	-	-
8	H	1.64	6.08	0.27
9	I	3.26	8.08	0.40
10	J	12.64	6.53	1.94
11	K	4.66	3.25	1.43
12	L	9.40	5.40	1.74
13	Cellulose Acetate	14.28	3.08	4.64
14	Cellulose	0.00	8.70	0.00

Besides, changes in the stretching band of C=O carbonyl, it was observed that the O-H spectrum from alcohol functional group at $3300\text{-}3400\text{ cm}^{-1}$ is decreased.

Cellulose Acetate Morphologies

Surface structure of cellulose, acetylated cellulose and

cellulose acetate commercial was studied. Fig. 3 shows the diameter of pure cellulose, method F and method J. Method F and J were the best methods of this study. It was observed that the diameter fibre of cellulose method F and J decreased compared to the pure cellulose. The pure cellulose diameter ranges from 26 to $29.9\mu\text{m}$. Meanwhile, acetylated cellulose

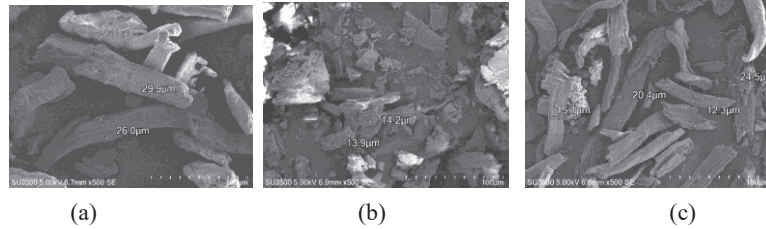


Fig. 3: SEM micrograph for commercial cellulose (a), acetylated cellulose method F (b) and acetylated cellulose method J (c).

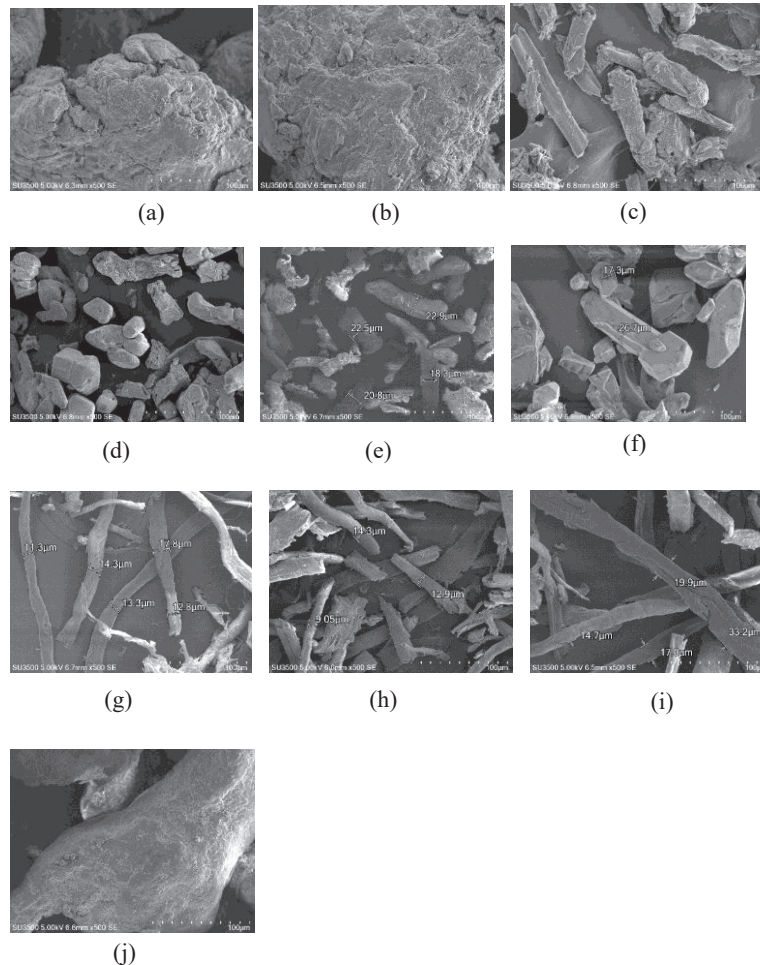


Fig. 4: SEM micrograph for acetylated cellulose A method (a), B method (b), C method (c), D method (d), E method (e), G method (f), I method (g), K method (h), L method (i) and cellulose acetate commercial (j).

ranges from 13.9 to 14.2 μ m for F method and 12.3 to 25.5 μ m for the J method. There was a modification in cellulose surface structure following esterification.

Meanwhile, other cellulose acetate resulted from other methods showed varying diameter and is presented in Fig. 4. Based on Fig. 4, it showed that acetylation process influence the surface structure of cellulose fibre.

CONCLUSIONS

This study confirmed that the activation step in the synthesis of cellulose acetate is important. Meanwhile, the addition of trichloroacetate catalyst resulted in better peak ratio than that of catalyst in the conventional methods. Therefore, the addition of strong organic acid will improve the acetylation process. The important finding of this study is that iodine catalyst showed superior effect than that of all the catalysts and it is a promising catalyst agent in the production of cellulose acetate in the future.

ACKNOWLEDGEMENT

The authors acknowledge the Ministry of Research, Technology, and Higher Education of The Republic of Indonesia for the research grant Incentive Research National Innovation System Batch I, 2019.

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