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Cellulose Triacetate Synthesis from Empty Fruit Bunches of Oil Palm's Cellulose

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Abstract. There are 23% of oil palm empty fruit bunches (OPEFB) waste produced from every ton of oil palm every year. The cellulose content in OPEFB was 33,3% so that it can synthesize into cellulose triacetate has applications for dialysis membranes, film layers, and cinema films. Cellulose triacetate can be synthesized from cellulose from OPEFB using acetylation reaction. The purpose of this study was to determine the synthesis process condition of cellulose triacetate. This research, microcrystalline Cellulose (MFC)/acetic acid glacial and temperature system is used to synthesize cellulose triacetate with transesterification. Microcrystalline cellulose/Acetic acid glacial (10;17.5; 25), acetic anhydride and sulfate acid was preferred as raw material, catalyst and acetylation reactants respectively. Results of this reaction were characterized by Fourier Transform Infrared (FT-IR) spectroscopy and degree of acetylated to confirm the chemical structure of cellulose triacetate produced.

INTRODUCTION

Around 25 – 26 % of palm oil production is oil palm empty fruit bunch (OPEFB) waste. In the OPFEB waste still containing 33.25% cellulose, which can be applied as various products including cellulose triacetate [1]. Cellulose triacetate is a derivative of cellulose that has many applications for the separation process, drugs, optic film protector, textile, thermoplastic, cosmetics, and the others [2]. Cellulose triacetate can be synthesized by acetylation reaction of cellulose then for the acetylation process use H_2SO_4 as a catalyst [2]. Besides that, one type of resources that can use for synthesis cellulose triacetate is empty bunches coconut oil's cellulose [1].

Cellulose triacetate (CTA) can be made by the acetylation reaction method. There are two steps of acetylation reaction. The first is the activation process cellulose with an acid compound, and the second is the reaction process using acetic anhydride and sulfuric acid as a catalyst. According to the previous experiment, most all of experiment using acetylation reaction for cellulose triacetate synthesis [2-4].

Therefore, empty bunches palm oil's cellulose can be used for synthesis cellulose triacetate. Djuned et al., [5] have tried to synthesize cellulose from OPEFB into cellulose acetate. Cellulose acetate has less acetyl groups than cellulose acetate. While Ribeiro et al., [6] have synthesized CTA from sugarcane bagasse for drug delivery system purpose.

In this work, CTA was made through acetylation process with H_2SO_4 as catalyst, composition cellulose and glacial acetic acid variation, temperature process, and acetylation time variation. The objective of this research was to determine the composition of cellulose: glacial acetic acid and acetylation time. Making CTA from OPEFB with this method has never been done, so that it becomes an academic novelty that we present.

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MATERIALS AND METHOD

Materials

The cellulose from empty fruit bunches oil palm was obtained from Polytech Indonesia (South Tangerang, Indonesia). Sulfuric acid (98 %), glacial acetic acid (98 %), acetic anhydride (98 %) were purchased from Univar (Illinois, USA). All chemicals were used as received without further purification.

Acetylation of Empty Fruit Bunches of Oil Palm

Cellulose from acetylated palm oil empty fruit bunches using acetic anhydride as acylation agent, sulfuric acid as catalyst, and glacial acetic acid as solvent. A mixture of three different amounts of glacial acetic acid (10, 17.5, and 25 mL) and 1 gram of commercial cellulose made from OPEFB are placed into a glass. The mixture is then sterilized and heated with temperature variations (40, 50 and 60 °C) for 1 hour under atmospheric conditions. After that, a mixture of 5 mL acetic anhydride and 0.2 mL sulfuric acid was added to the system at 50 °C for 60 minutes, then stirred. The glass is then removed from the heater after the reaction process is complete and then soaked in cold water until white solids appear. The liquid solids are then separated through a filtration process, and the solids obtained are washed with distilled water until pH becomes neutral to remove anhydride, sulfuric acid, and unreacted acetic acid byproducts. The solid obtained is washed with distilled water until pH becomes neutral to remove anhydride, sulfuric acid, and unreacted acetic acid byproducts. The solid is then dried in an oven at 80 °C until the weight is constant. Each experiment is repeated in triplicate to minimize errors. The yield of cellulose triacetate determined by dividing the mass of product with the mass of raw material and multiplying with 100% as shown in equation (1) [4]

$$Yield = \frac{weight\ gain}{original\ weight} \times 100\% \quad (1)$$

Degree of Substitution Determination

FTIR spectra from Spectrum Two TM Infrared Spectrometer Perkin Elmer (Massachusetts, USA) was used for test carbonyl and hydroxyl element of the sample at ambient temperature. The range of wavenumber between 400 cm^{-1} and 4000 cm^{-1}. The result of FTIR can be used for determining the percentage of the acetyl group and the degree of substitution (DS). DS of the sample obtained was calculated from the ratio between the absorbances of C=O stretching (1750 cm^{-1}) and OH (3400 cm^{-1}). The ratio between these absorbances is related to the percentage of acetyl groups (% AG). The value of the percentage of acetyl groups relates to DS according to equation (2) and (3) [7].

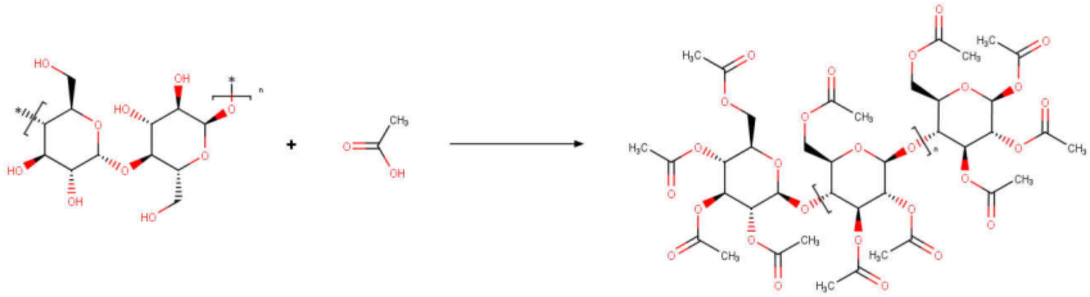
$$\%AG = 43.69(1 - e^{-0.947x})^{2.153} \quad (2)$$

where x = ratio between the absorbances of the drawstring C=O (1750 cm^{-1}) and OH (3400 cm^{-1}).

$$DS = \left(\frac{162 \times \%AG}{4300 - 42 \times \%AG}\right) \times 100 \quad (3)$$

RESULTS AND DISCUSSION

The chemical reaction of cellulose from empty bunches palm oil is represented in the reaction scheme 1, where Cellulose-OH represents the hydroxyl groups present on the polymeric component of cellulose from empty bunches palm oil. The acetic anhydride has to react mainly with the hydroxyl groups of cellulose.



SCHEME 1. Cellulose Triacetate production from OPEFB cellulose and acetic acid

Effect of Ratio of Cellulose (MFC)/ Glacial Acetic Acid and Temperature on Degree of Substitution

Fig. 1 shows the effect of composition ratio and acetylation temperature on DS. There was no significant change on DS. This phenomenon is due to the reaction was already in the equilibrium state [8]. Then, the composition ratio 1 : 17.5 (gr/mL) has the higher DS than the others because the amount of glacial acetic acid and temperature 50 °C were enough to make the cellulose swelling (increased surface area of cellulose) and the intermolecular hydrogen bonds decreased. Therefore, cellulose will be reacted easier, and hydroxyl groups of cellulose will be substituted with acetyl groups [9]. Furthermore, DS for composition ratio 1 : 10 (gr/mL) was a little bit lower than 1 : 17.5 (gr/mL). Next, the DS for composition ratio 1: 25 was lower than the others due to the more glacial acetic acid caused the condition of reaction under strong acid so the cellulose will be degraded [8].

The result of DS is shown in Fig. 1. The ratio of 1:10, DS value of 40 ˚C, 50 ˚C, and 60 ˚C reached 0.56, 2.84, and 1.1 respectively. The ratio of 1:17,5, DS value of 40˚C, 50˚C, and 60˚C reached 2.86, 2.87, and 2.87 respectively. The ratio of 1:25, DS value of 40˚C, 50˚C, and 60˚C reached 0.31,0.08, and 0.28 respectively. The minimum DS value is obtained from the ratio of 1:25 and 1:10. Then the highest DS value is obtained from the ratio of 1:17.5 and the temperature of 50˚C. Therefore, cellulose (MFC)/ Glacial Acetic acid ratio of 1:17.5 have the maximum DS value because this ratio has an ideal volume of glacial acetic acid. The mass ratio of cellulose and acetic acid glacial has affected to DS value. Increasing the concentration of glacial acetic acid can cause degradation of carbohydrates, which is decreased weight and percentage of acetyl content [10]. In addition, the ideal volume of glacial acetic acid helps swell cellulose to improve the reaction surface area. The temperature of acetylation has affected to DS Value. The DS value of 40 ˚C has obtained the highest DS on the ratio of 1:17.5. The DS value of 50 ˚C has obtained the highest DS value on the ratio of 1:10 and 1:17.5. The temperature of 60 ˚C has obtained the lowest DS value. Sulfuric acid oxidized strongly that can make sulfuric acid dehydrate [8]. The temperature of 50 ˚C is the optimum temperature for heterogenous reaction of cellulose triacetate [8]. It shows the DS value of Cellulose (MFC) and glacial acetic acid of 1:17.5 at the temperature of 50 ˚C reached 2.87 closes to 2.9 was obtained cellulose triacetate.

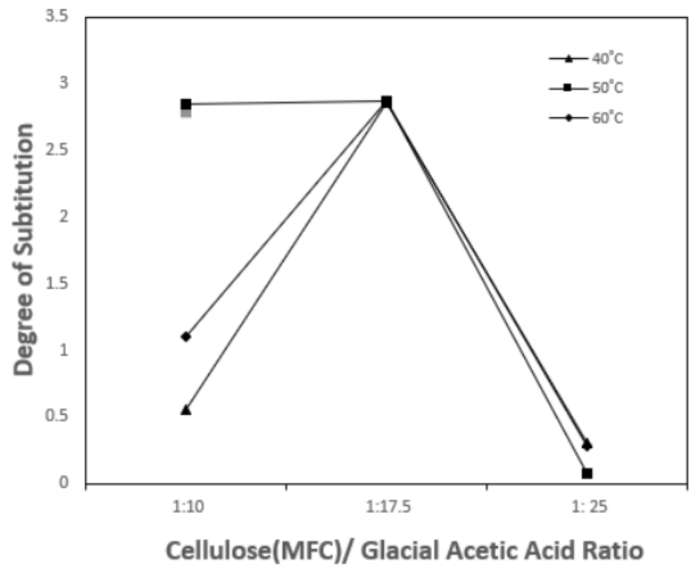


FIGURE 1. Degree of Substitution from different cellulose/Acetic acid ratio under various temperature

Effect of Ratio of Cellulose (MFC)/ Glacial Acetic Acid and Temperature on Yield Cellulose Triacetate

Fig. 2 shows the effect of composition ratio and temperature on yield cellulose acetate. On the ratio of 1:10, the yield percentage of 40 ˚C, 50 ˚C, and 60 ˚C respectively reached 116.16%, 129.09%, and 69.59%. On the ratio of 1:17.5, the yield percentage are 109.14%, 98.8%, and 81.69%. The ratio of 1:25, the yield percentage of 40 ˚C, 50 ˚C, and 60 ˚C respectively reached 62.84%, 81.67%, and 106.22%. Fig 4 indicated that the ratio of 1:10 at 40 ˚C and 50˚C has obtained the highest yield percentage than the ratio of 1:17.5 and 1:25. The temperature of acetylation also has an effect on the yield percentage. The ratio of 1:10 has obtained the highest yield but unwanted products are also produced. The unwanted product will be produced when the condition of acetylation especially is not required. The 1:25 ratio has the lowest yield percentage of 40˚C and 50˚C, but at 60˚C the highest yield percentage is obtained. Increasing the concentration of glacial acetic acid can cause carbohydrates degradation which decreases the increase in weight and percentage of acetyl content.

Fig. 2 shows the temperature relationship between the effect of the cellulose/glacial acetic acid ratio and the temperature of acetylation. There is a correlation between cellulose/ glacial acetic acid ratio and temperature of acetylation, which the effects of DS value [10]. Fig. 1 shows the DS value closes to 2.89 at the ratio of 1:10, 1:7.5, and 1:17.5 under temperature 50 ˚C. The higher temperature of acetylation decreases cellulose swelling rate [8] and oxidase catalyst [10]. At the temperature of 40 ˚C, high yield is obtained, this is a partial product of sulfonation-acetic-cellulose, sulfonation during the acetylation process [8]. The DS value and percentage yield value must be considered to decide on the optimal process. From Figure 1 and Figure 2, the optimal acetylation of cellulose triacetate ratio is 1:17.5 at 50 ˚C.

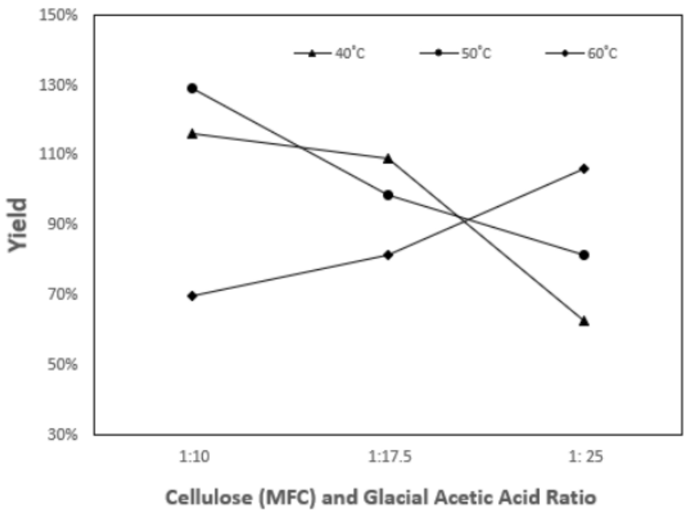


FIGURE 2. Yield percentage from different cellulose/Acetic acid ratio under various temperature

CONCLUSION

The present study reported the acetylation of cellulose triacetate and the characterization of MFC (Micro-Fiber Cellulose) which is cellulose from palm oil empty fruit bunches using acetic anhydride as acetyl donor, glacial acetic acid as solvent of cellulose, and sulfuric acid as catalyst. The optimum condition of the acetylation process was decided by two parameters, percentage yield and DS (Degree of Substitution) of cellulose triacetate. From these considerations, the ratio of cellulose (MFC) to Acetic Glacial Acid (gram/ mL) was 1:17.5, and the acetylation temperature is 50˚C as the optimum condition of the acetylation process. The ratio of 1:17.5 is the ideal ratio of cellulose (MFC) as a swelling agent to enlarge the surface area for the reaction process and prepare carbonyl function group bonding on the cellulose crystalline structure. The temperature of 50 ˚C was the optimum temperature for the heterogeneous reaction of cellulose triacetate. The yield of cellulose triacetate was obtained 98.8%. This study identified that the product was cellulose triacetate, and the degree of acetyl substitution was 2.87 that closes to 2.9. These results indicating successful of acetylation reaction to transform cellulose to become cellulose triacetate.

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