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Synthesis of cellulose acetate from palm oil bunches and dried jackfruit leaves

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Abstract. Cellulose acetate is a natural polymer, that is widely used in various industries, especially fiber and plastics. Cellulose acetate was created by an esterification reaction of cellulose and acetic anhydride. The raw materials used in this research were empty fruit bunches of palm oil and dried jackfruit leaves, because utilization of waste, available in large quantities, and contain high cellulose. The objective of this study was to obtain high yield cellulose and cellulose acetate from palm oil bunches and jackfruit leaves. This was done by variating delignification time, bleaching time, and acetylation time. Cellulose isolation was performed through a delignification process by adding NaOH and bleaching process by adding H_2O_2. The optimum yield for the empty palm oil bunches cellulose was 36.45%, with the delignification time of 1.5 hours and the bleaching time of 30 minutes. The optimum yield of jackfruit leaves cellulose was 13.72%, with 1-hour delignification time and 30 minutes bleaching time. Cellulose acetate was obtained by cellulose activation process by adding acetic acid glacial, acetylation process with anhydrous acetate, and hydrolysis with water. The yield of cellulose acetate obtained was 81.75% for palm oil bunches and 63.89 for jackfruit leaves.

1 Introduction

Cellulose acetate is a natural polymer, that is widely used in various industries, especially fiber and plastics. For example, as yarn in the textile industry, filter on cigarette, material for plastic, film, and paint (Kirk & Othmer, 1977). It was made from cellulose by acetylation process. Cellulose could be isolated from plants or biomass. Empty palm oil bunches (EPOB) and dried jackfruit leaves (DJL) are two sources of biomass that is available in Indonesia.

Indonesia is one of the countries with the largest palm oil plantations in the world. Therefore, many palm oil factories are established in Indonesia and produce a lot of empty bunches of palm oil. Empty palm oil bunches are the biggest waste in processing palm into palm oil. The average production of empty palm oil bunches is 20-23% of total oil palm production in Indonesia (Wardani & Widiawati, 2012). The content of cellulose in empty palm oil bunches is 38.76% (Bahmid *et al.*, 2013).

In addition to palm oil bunches there is another potential material, that is jackfruit leaves. Indonesia is a tropical country so it's suitable to grow plants, including jackfruit plant. This plant is found in almost all parts of Indonesia and is favored by most people. Even so, the used of jackfruit is limited to the fruit alone. In addition to the fruit, the other parts are just thrown away. Only a small percentage of people use jackfruit leaves as traditional scrubs. It is very good for skin because it can remove black spots, acne scars, and dead skin. Therefore, jackfruit leaves will be used for cellulose acetate raw materials. The cellulose content of dried jackfruit leaves is 21.45% (Sasongko *et al.*, 2010).

2 Experimental

2.1 Preparation

Raw materials (EPOB and DJL) were taken from tree, cleaned, and washed. Then EPOB and DJL were dried in the sun to reduce water content and obtained dried materials. After that, it was cut to smaller pieces (about 2cm), making raw materials easier to process.

2.2 Cellulose

The isolation of cellulose from raw materials EPOB and DJL began with heating two grams of raw materials in 40 mL of 17.5% NaOH solution at 90-100^oC for ½, 1, 1½, 2, or 2½ hours. Then it was washed repeatedly using aquades until the pH was neutral. After that, the sample was heated in 20 mL of 10% H_2O_2 at 80-90^oC for 15, 30, 45, 60, or 75 minutes. Cellulose was then filtered and washed with aquades, then dried in an oven at 105^oC for 6 hours to get low moisture cellulose.

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2.3 Cellulose Acetate

The synthesis of cellulose acetate began with mixing acetic acid glacial and cellulose with a ratio of 1:20 (w/v). The solution was stirred for one hour to activate cellulose before reacting with acetic anhydride. Then H_2SO_4 as a catalyst was added to the solution. Subsequently, acetic anhydride was added with a ratio of cellulose and acetic anhydride 1:10 for EPOB and 1:5 for DJL. The solution was stirred for 30, 45, 60, 75, or 90 minutes so the acetylation process begins. After that, aquades was added with the ratio of 2:1 (aquades : acetic acid glacial) and stirred for 30 minutes, so the acetylation stops and hydrolysis starts. Cellulose acetate was then filtered and washed with aquades, then dried in an oven at 105°C for 6 hours.

3 Results and discussion

3.1 Cellulose

Cellulose in this study was isolated using delignification and bleaching process with variations of process duration. First, the delignification process dissolved the impurities like hemicellulose and lignin. Delignification using 17.5% NaOH because it's the largest concentration that would dissolve impurities without dissolving cellulose. During this process, the solution turned brown until it eventually became dark brown. This was due to the oxidation reaction of phenolic compounds from the decomposition of lignin by air.

After the delignification process, cellulose was bleached by soaking it in H_2O_2. Cellulose that was dark brown or black turned into yellowish white. The H_2O_2 bleaching agent is a HOO- (perhydroxyl radical), formed by ionization in water. The ionization reaction of H_2O_2 in water can be seen in equation (1)

$$H_2O_2 + H_2O \rightarrow H^+ + HOO^- \qquad (1)$$

Bleaching occurs when highly unstable HOO^- ions decompose due to oxidizable substance, which was a pigment in cellulose. It was heated to make the HOO^- ions more unstable so bleaching runs faster. After bleaching, the cellulose became yellowish-white fibers.

The effect of delignification time on cellulose yield can be seen in Fig. 1.

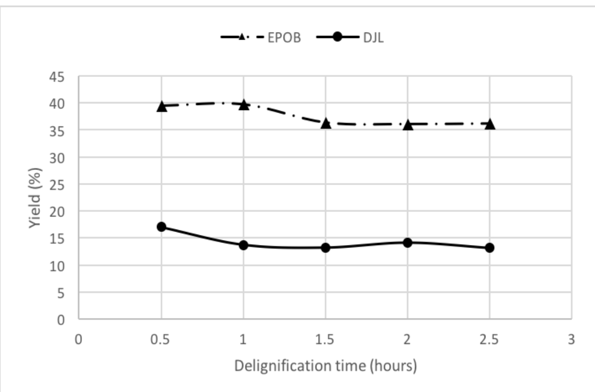

Fig. 1. Effect of delignification time on the cellulose yield.

From Fig. 1, it can be seen that for EPOB at 0.5 and 1 hour, the yield is higher than cellulose at 1.5, 2, and 2.5 hours. This shows that there is no significant difference between 1.5 to 2.5 hours for EPOB cellulose. As for DJL cellulose, high yield was generated at the time of 30 minutes then decreased and become stable from 1-2.5 hours. The yield stability was caused by all impurities has been dissolved, resulting pure cellulose and it could not be purified even when the delignification time was longer. Pure cellulose was obtained at the time of 1.5 hours for EPOB and 1 hour for DJL. Pure EPOB cellulose obtained with a yield about 36% and DJL about 13%.

In addition to delignification variation, there was also variation of bleaching time to find the most efficient time for cellulose production. The graph of bleaching time effect on cellulose yield produced can be seen in Fig. 2.

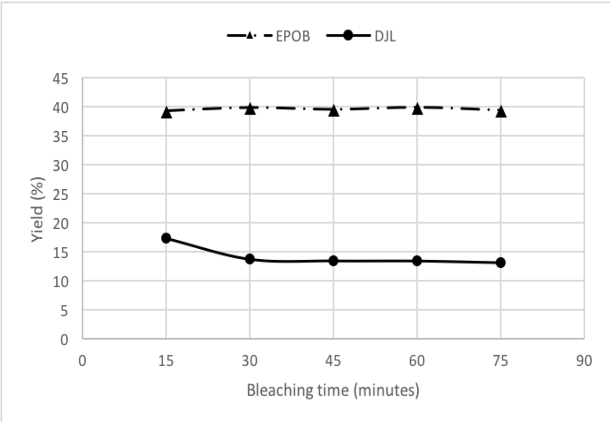

Fig. 2. Effect of bleaching time on the cellulose yield.

The figure above shows that the duration of bleaching does not affect the yield of EPOB cellulose. However, when the bleaching time was only 15 minutes, some pigment is still there, resulting cellulose still slightly black. Starting from 30 minutes, all pigment was already dissolved so it produced white cellulose fibers.

For DJL cellulose, bleaching time does not affect the color because the pigment dissolved fast. However, bleaching makes the remaining impurities dissolved. Fig. 2 shows that the cellulose yield is still high at 15 minutes, but after that it becomes constant with 13% yield.

3.2 Cellulose Acetate

After obtaining cellulose, the making of cellulose acetate could begin. Cellulose acetate synthesis started with the activation of cellulose by acetic acid glacial. During the activation process, the cellulose structure inflated and made the surface area larger and the intermolecular hydrogen bonds decreased. Therefore, cellulose reacted easier and binded acetyl groups during acetylation process.

Furthermore, acetic anhydride and H_2SO_4 as a catalyst were added. While the acetylation process occurs, it just needed to be stirred and did not need to be heated, because it was an exothermic reaction. Low temperatures prevented damaging the cellulose acetate chain that had formed and prevented gel formation. The reaction process was sulfuric acid catalyst reacting with acetic anhydride to form acetyl sulfate, then reacted with cellulose to produce cellulose acetate. Thus, the cellulosic hydroxyl group would be replaced by an acetyl group. The reaction can be seen in equation (2)

$$C_6H_7O_2((OH)_3)_{x(s)} + 3_x(CH_3CO)_2O_{(l)} \rightarrow C_6H_7O_2((OCOCH_3)_3)_{x(s)} + 3_xCH_3COOH_{(l)} \quad (2)$$

Cellulose + acetic anhydride → cellulose acetate + acetic acid

The next step was hydrolysis, started when water was added. This process makes the solution colored change from clear brown to turbid white. The white color indicated the cellulose acetate that formed into solids. The cellulose acetate produced was in a form of a brownish white powder.

The effect of acetylation time on cellulose acetate yield can be seen in Fig. 3.

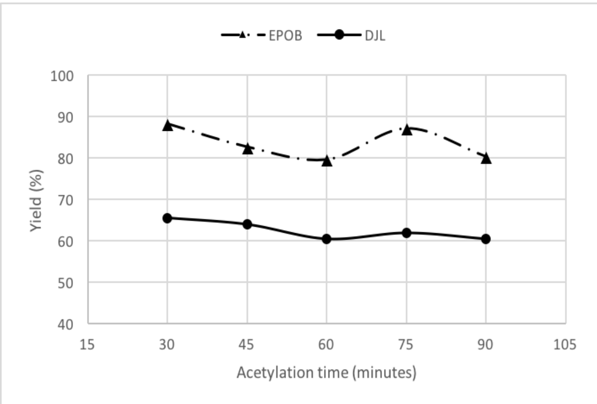

Fig. 3. Effect of acetylation time on the cellulose acetate yield.

The cellulose acetate formed at 30 minutes was mainly unable to become powder. That's because of not all cellulose had reacted with acetic anhydride. Thus, the product was not all cellulose acetate, but a mixture of cellulose acetate and cellulose.

EPOB cellulose acetate apart from 30 minute acetylation time, was very easy to become powder. The graph shows that yield keeps rising to its peak when the acetylation time is 75 minutes, then falls down. This is in accordance with the theory that the longer the acetylation time, the higher the yield. Due to the esterification process increased so that the amount of acetyl and cellulose acetate weight increased (Bahmid, 2014). However, at some point the yield would decrease because cellulose and cellulose acetate were degraded by the solvent (Asnetty, 2007).

DJL cellulose acetate had a different yield from EPOB. The effect of acetylation time was not significant for DJL cellulose. However, cellulose acetate which was very easy to become powder is cellulose acetate at 45 minutes acetylation. Whereas after 45 minutes acetylation time, cellulose acetate was more difficult to become powder. This occurs because the longer acetylation time, the acetyl in the cellulose acetate structure increase. Therefore, cellulose acetate structure had different properties and different functions. In addition, structural degradation occurred to glucose acid (Savitri *et al*., 2003).

4 Conclusions

This study obtained the best delignification time and bleaching time to isolate pure cellulose from palm oil bunches and dried jackfruit leaves. This study also obtained the best acetylation time to produce cellulose acetate from palm oil bunches and dried jackfruit leaves.

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