Synthesis of Cellulose Acetate from Rice Husk Cellulose by Ultrasound-Assisted Acetylation

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Cellulose acetate is an important product derived from cellulose. Cellulose acetate can be used in a variety of applications including coatings, textile fibers, consumer goods, filtration membranes, composites, laminates, pharmaceutical, and medical items. Rice husk is a lignocellulosic material that contains cellulose and hemicellulose. The aims of this study were to determine the effect of process variables on the cellulose acetate product formation by ultrasound-assisted acetylation using iodine as a catalyst and to characterize the cellulose acetate product. The research was conducted through the delignification, bleaching, acetylation, and characterization processes. The results showed that the optimum yield of cellulose acetate was obtained at the temperature of 60 °C, the reaction time of 50 min, the weight of the catalyst of 10% of cellulose weight, and the ratio of cellulose and acetic anhydride of 1:5 (w/v). The acetylation process using iodine as a catalyst with an ultrasound-assisted method was more effective than the conventional acetylation (acetic acid glacial and sulfuric acid as a catalyst).

DOI: 10.15376/biores.18.3.4688-4698

Keywords: Rice husk; Cellulose; Cellulose acetate; Ultrasound assisted; Acetylation

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INTRODUCTION

Indonesia is an agricultural country. Rice is one of the main agricultural products as the staple food for Indonesian people. Such usage of rice leaves the rice husk unused. Recently, the rice husk has not been used properly. Rice husk is a lignocellulosic material that contains a lot of cellulose. Rice husk has cellulose and hemicellulose contents of 32.67% and 31.68%, respectively (Ma'ruf *et al*. 2017; Laghari *et al*. 2018). Cellulose and hemicelluloses can be processed further for bio-ethanol production by hydrolyzing them into monomeric sugar and cellulose acetate by the acetylation process (Hindi and Abohassan 2015). One of the most significant cellulose derivatives is cellulose acetate (CA). Cellulose acetate has been used in various products, including coatings, textile fibers, consumer goods, filtration membranes, composites, laminates, pharmaceuticals, and medical items.

The utilization of rice husks as a source of cellulose must begin with a delignification process. The delignification process aims to remove lignin from rice husks. Because rice husk also contains silica, the delignification process also removes the silica content in rice husk (Ma'ruf *et al.* 2017). There are several delignification methods,

such as acid delignification, alkali delignification, physical delignification, organic solvent delignification, and microbial delignification (Park *et al*. 2015; Jung *et al*. 2018; Minmunin *et al*. 2018; Gunam *et al*. 2020; Yu *et al*. 2022). In this research, the delignification process was done with alkali at high temperatures using an autoclave. Islam *et al*. (2017) reported that the low-pressure alkaline delignification (LPAD) effectively removed impurities (lignin and silica) and increased the content of cellulose from 35% to 97%.

The conventional acetylation process using acetic anhydride usually was conducted at a temperature of 40 °C for 8 h. The time of acetylation can be reduced to 5 h by increasing the temperature to 80 and 120 °C using an autoclave (Maryana *et al*. 2020). As an effort to intensify the process, an acetylation process has been carried out using a microwave (Li *et al*. 2009). The acetylation using microwave irradiation was conducted at the power of irradiation of 300 to 800 W, a reaction time of 5 to 40 min, and a reaction temperature of 80 to 130 °C. The acetylation using microwave heating can reduce the energy consumption, solvent, and amount of catalyst quantities (Li *et al*. 2009; Eranna *et al*. 2015).

The utilization of ultrasound for process intensification has been done by several researchers. A large number of organic reactions can be carried out under ultrasonic irradiation in high yields, short reaction times, and mild conditions (Mohamed 2016). Truong *et al*. (2018) successfully synthesized furic acid from γ-oryzanol by a homogeneous reaction assisted by ultrasound. Additionally, Ratnawati *et al.* (2016) used ultrasonic irradiation for the depolymerization of k-carrageenan.

This study aimed to determine the effect of process variables on cellulose acetate formation by ultrasound-assisted acetylation and to characterize the CA product. Effects of three process variables, the temperature, time, and weight of the catalyst, were evaluated. The characteristics of CA are analyzed using Fourier transform infrared (FTIR) spectrometry and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Rice husk was purchased from a local rice milling factory at Banyumas (Jawa Tengah, Indonesia). Hydrogen peroxide solution (30%), acetic anhydride, iodine, sodium thiosulfate pentahydrate, and sodium hydroxide were obtained from Merck (Darmstadt, Germany). Ethanol (70%) was obtained from Bratachem (Purwokerto, Indonesia). Demineralized water was produced by Elva-Veolia Technology (Celle, Germany).

Delignification

The alkali delignification process of rice husk was conducted using 1.0 M sodium hydroxide solution. The ratio of the weight of the rice husk to the volume of solution was 1:10. Delignification was completed using an autoclave at the temperature of 121 °C and 15 min. After the delignification process, the rice husk was washed using demineralized water until a pH of 7 and then dried at a temperature of 105 °C for 6 h in the oven.

Bleaching

After the delignification process, the crude rice husk cellulose obtained was bleached using a hydrogen peroxide solution of 2%. The bleaching process was

completed at the temperature of 40 °C for 2 h. After the bleaching process, the rice husk cellulose was washed using demineralized water until a pH of 7 and then dried at a temperature of 105 °C for 6 h in the oven.

The rice husk cellulose was crushed after bleaching and sieved until the particle size of 40 to 60 mesh was achieved.

Acetylation

Acetylation of rice husk cellulose was done using an ultrasound bath (Fig. 1). About 2 g of rice husk cellulose was dissolved in 10 mL of acetic anhydride. Iodine as a catalyst was added with an amount of 0.2 g. The acetylation process was conducted at a temperature of 50 °C for 30 min. The experimental design can be seen in Table 1.

Fig. 1. Ultrasound bath used for the acetylation process

After acetylation was completed, the mixture was cooled until room temperature was achieved. The mixture was then mixed with 5 mL of sodium thiosulphate solution and stirred until the color of the iodine disappeared. About 30 mL of 70% ethanol was added to the reaction mixture and stirred for 30 min. The mixture was then filtered using filter paper. The CA produced was then washed using water and dried at the temperature of 60 °C for 6 h. The dried CA was weighed, and its yield was calculated using Eq. 1,

$$\text{Yield} = w_1/w_0 \times 100\% \quad (1)$$

where w_1 (g) is the dry weight of CA and w_0 (g) is the dry weight of rice husk cellulose.

Table 1. Experimental Design of Acetylation Process

Variables	Range			
Temperature (°C)	40	50	60	70
Time (min)	30	40	50	60
Weight of catalyst (g)	0.1	0.2	0.3	0.4

Characterization

The cellulose and CA were analyzed using Fourier transform infrared (FTIR, (Shimadzu, Kyoto, Japan)) spectroscopy. FTIR analysis used a KBr pellet. The KBr pellets consisted of 300 mg KBr and 0.1 mg fine powder of sample. Scans were recorded from 400 to 4000 cm^{-1} at a resolution of 16 cm^{-1}. The morphology of CA was examined using the scanning electron microscope (SEM, (JEOL, Tokyo, Japan). The magnification of SEM analysis was 5000x.

RESULTS AND DISCUSSION

Characteristics of Rice Husk Cellulose

Rice husk is a lignocellulosic material that contains the three main chemical components—lignin, cellulose, and hemicellulose. To isolate the cellulose, the delignification process must be done. Alkali delignification at high temperature (121 °C) is effective for eliminating lignin. At the temperature of 121 °C, 15 min, and using 1:10 ratio of rice husk weight to NaOH (1 M) volume, the yield of cellulose obtained was 84.8%. The amount of lignin eliminated reached 15.2%. Based on previous research (Ma'ruf *et al*. 2017), the content of lignin was 18.8%, and the percentage of lignin removed was 81.0%. This result is higher than that obtained by Minmunin *et al.* (2018) in the delignification process of bana grass using sodium hydroxide and ozone, which only reached 63.4%. Meanwhile, Jung *et al.* (2018) in the delignification process of switchgrass using microbial delignification process achieved 84.3%.

The functional groups of rice husk cellulose were analyzed using FTIR. Figure 2 shows the FTIR spectra of rice husk cellulose. The peak at 1153.4 cm^{-1} shows the antisymmetric stretching of the C-O group in cellulose. The peak of 1029.99 cm^{-1} shows the C-O-C pyranose ring skeletal vibration. The peak at 898.8 cm^{-1} shows the C-H rocking vibration (Reddy *et al*. 2012). The peak of 3336.8 cm^{-1} and 2892.4 cm^{-1} show the stretchings of H-bonded –OH groups and methyl and methylene units. Rice husk has a high content of silica, but the wavenumber of 722 cm^{-1} and 817 cm^{-1} (Si-C bond) are not found, the cellulose obtained had no content of silica (Omar *et al*. 2012)

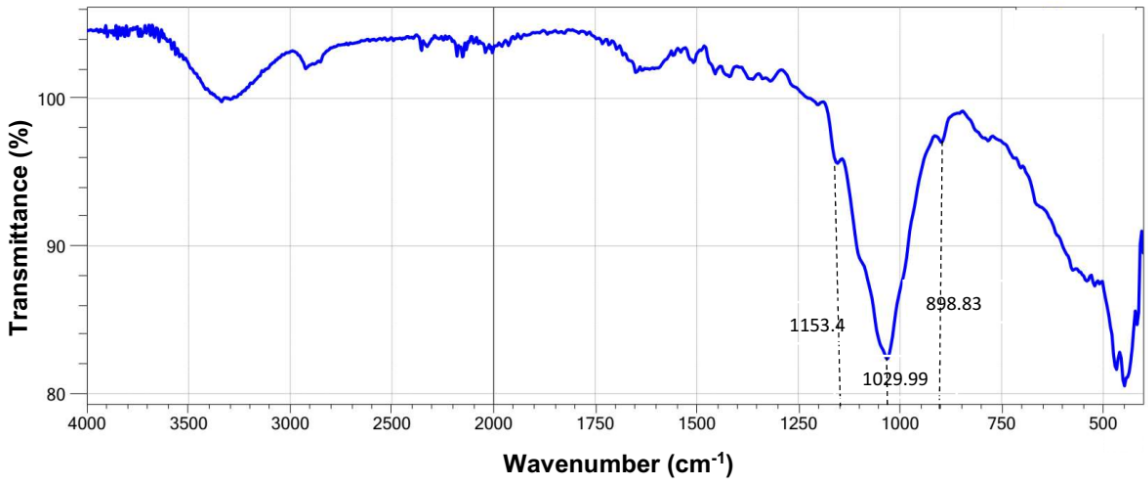

Fig. 2. FTIR spectra of rice husk cellulose

Figure 3 shows the morphology of rice husk cellulose. Natural cellulose fibers are multicellular, according to Reddy *et al*. (2012), where lignin and hemicellulose bind as a bundle of different cells. The majority of the lignin and hemicellulose were eliminated following the chemical processing, and the raw fiber's cellulose microfibrils were then dispersed to create fibrils. The recovered cellulose contains ribbon-shaped, short fiber strands with diameters ranging from 3 to 12 µm that are organized in irregular pieces and network form.

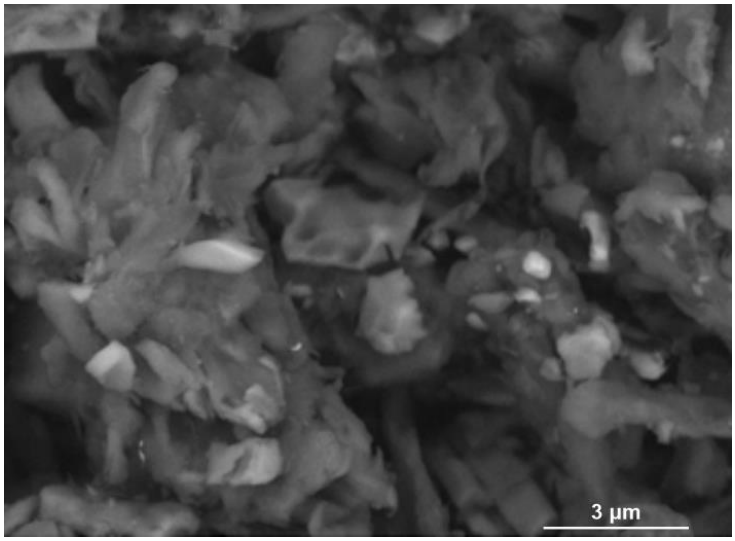

Fig. 3. Morphology of cellulose from rice husk

Effect of Temperature

Figure 4 shows the yield of CA obtained at various temperatures. The yield ranged from 55% to 95% based on the weight of the cellulose reacted. In general, it can be said that the yield of CA will increase at a higher temperature. However, there was a temperature limitation at 70 °C, according to the equipment used. Hindi and Abohassan (2015) on the production of cellulose triacetate from cotton fibers reported that the yield of acylated products reached 112% (glacial acetic acid activation, H_2SO_4 catalyst). Furthermore, it can be seen that the type of cellulose raw material and acetylation process will affect the yield of CA obtained. The maximum yield of the acylated product by ultrasound assisted-acetylation was larger than that obtained from glacial acetic acid activation.

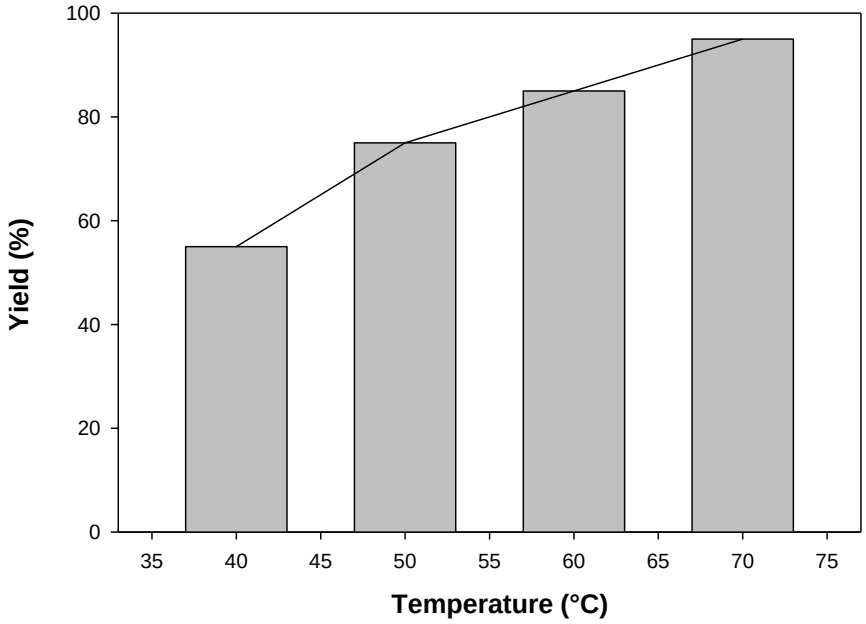

Fig. 4. The yield of cellulose acetate at various temperature (time 30 min, catalyst 0.2 g)

Effect of Time of Reaction

Figure 5 shows the yield of CA obtained at various reaction times. The yield ranged from 85% to 125% based on the weight of the cellulose reacted. In the time of 30 to 50 min, the yield increase was quite high (23.5% from 30 to 40 min, 14.3% from 40 to 50 min), but at 50 to 60 min, the CA yield increase was relatively small (4.2%). The time of reaction with the ultrasound-assisted method was reduced because of the cavitation energy during the reaction process. Figure 6 shows the mechanism of cavitation energy formation. Every cycle begins with the formation of bubbles with a diameter of 25 µm, the bubbles will grow, and at a diameter of 150 µm, the bubbles will burst. This cycle will repeat quickly, resulting in a large cavitation energy, which causes the frequency of collisions between cellulose and acetic anhydride to increase (Gharat and Rathod 2020).

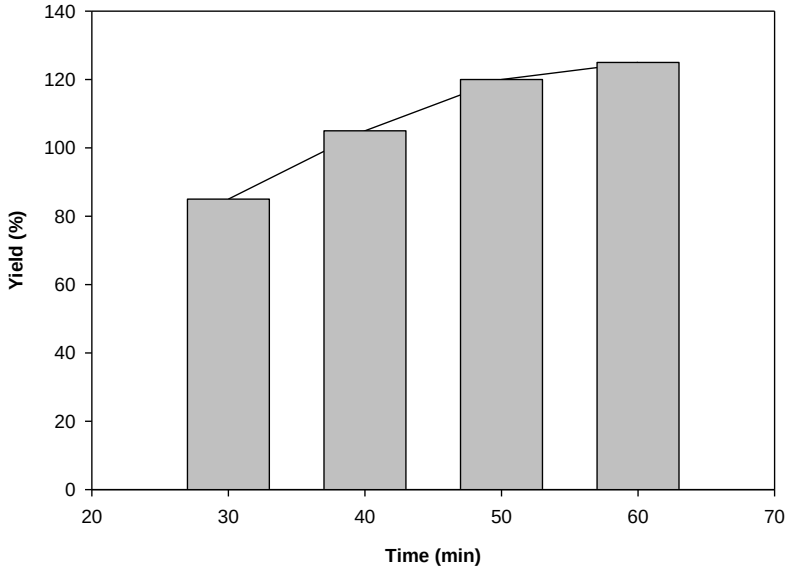

Fig. 5. The yield of cellulose acetate at various reaction time (temperature 60 min, catalyst 0.2 g)

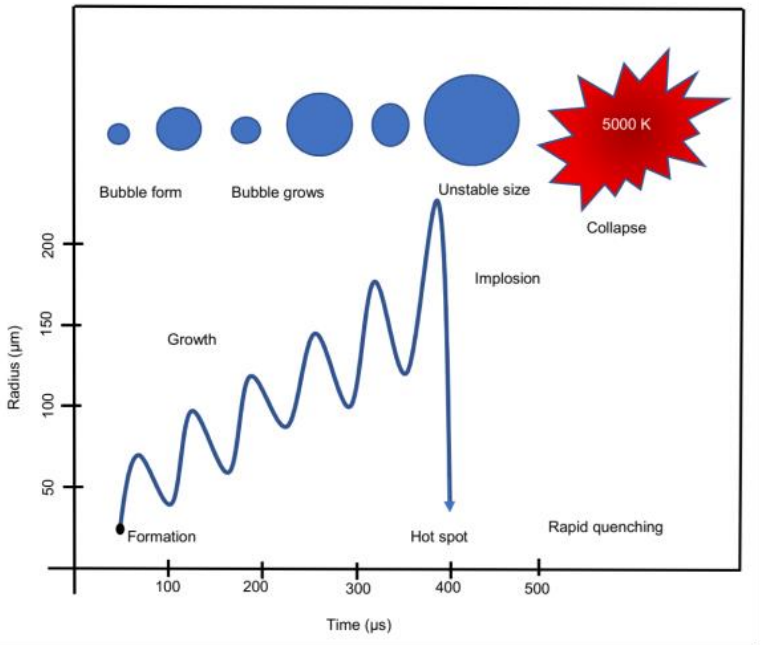

Fig. 6. Cavitation energy during the ultrasound-assisted reaction (Reprinted from Gharat and Rathod 2020 with permission from Elsevier)

Effect of Catalyst Weight

Figure 7 shows the yield of CA obtained using various weights of catalyst. The yield ranged from 105% to 125% based on the weight of the cellulose reacted. The optimum weight of the iodine catalyst was 0.2 g (10% of cellulose weight) at the ratio of cellulose and acetic anhydride was 1:5 (w/v). The yield of CA raised the optimum value of 120%.

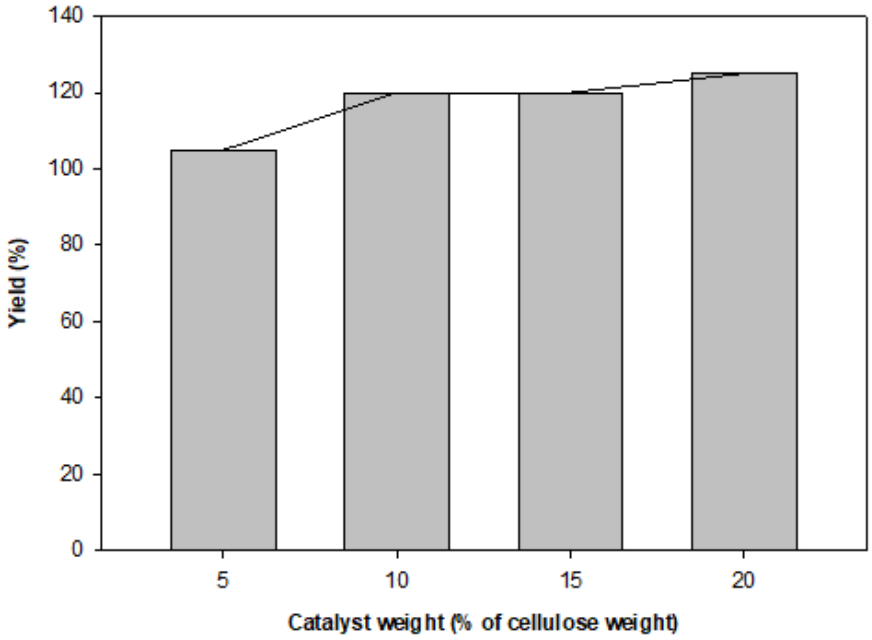

Fig. 7. The yield of cellulose acetate at various catalyst weight (temperature 60 min, time 50 min)

Figure 8 shows the mechanism of the reaction between cellulose and acetic anhydride with iodine as a catalyst with cavitation energy (CE)-assisted. In the first step, the iodine ion will break the carbonyl bond (C=O) in acetic anhydride. In the next step, the unstable C-O bonds will bind with O-H in cellulose to form cellulose acetate. The cavitation energy of the ultrasound bath helps to weaken the carbonyl bond so that the yield of CA can increase relatively high.

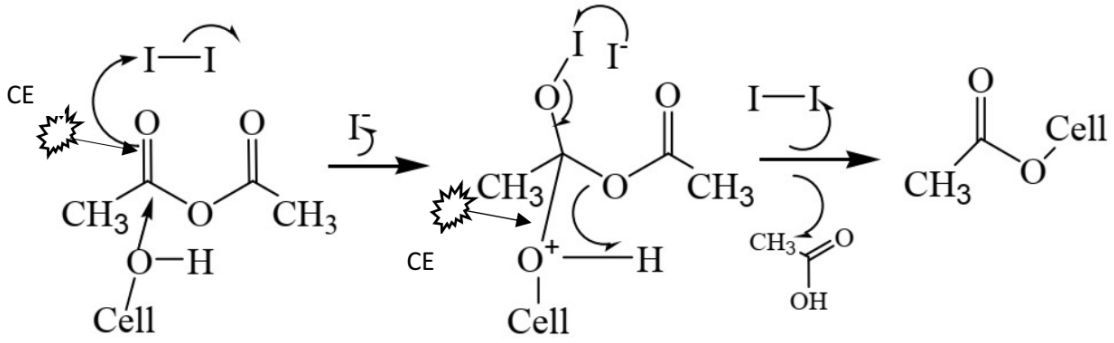

Fig. 8. Mechanism of acetylation using iodine as a catalyst with cavitation energy (CE)-assisted

The acetylation process using an iodine catalyst with an ultrasound-assisted method was found to be more effective than the conventional acetylation process (using glacial acetic acid activation and sulfuric acid as a catalyst). Table 3 shows the yield of CA obtained from different raw materials and processes.

Table 3. Cellulose Acetate Yield using Various Raw Materials and Processes

Raw Material	Acetylation Process	Conditions	Yield (%)	Reference
Cotton fibers	Glacial acetic acid activation, H_2SO_4 catalyst	T = 55 °C, t = 1 h	112.18	Hindi and Abohassan 2015
Recycled writing papers	Glacial acetic acid activation, H_2SO_4 catalyst	T = 55 °C, t = 1 h	94.43	Hindi and Abohassan 2015
Recycled newspapers	Glacial acetic acid activation, H_2SO_4 catalyst	T = 55 °C, t = 1 h	84.37	Hindi and Abohassan 2015
Barley straw	Glacial acetic acid activation, H_2SO_4 catalyst	T = 40 °C, t = 3 h	88.4	Jo *et al*. 2016
Rice straw	Glacial acetic acid activation, H_2SO_4 catalyst	T = 40 °C, t = 3 h	88.1	Jo *et al*. 2016
Oak wood	Glacial acetic acid activation, H_2SO_4 catalyst	T = 40 °C, t = 3 h	151.7	Jo *et al*. 2016
Palm trees	Glacial acetic acid activation, H_2SO_4 catalyst	T = 30 °C, t 18 h	94.5	Saikh *et al*. 2022
Rice husk	Iodine catalyst	T = 80 °C	66	Das *et al*. 2014
Commercial cellulose	Iodine catalyst, microwave irradiation	T = 130 °C	46	Li *et al*. 2009

Characterization of Cellulose Acetate

Figure 9 shows the FTIR spectra of CA from rice husk cellulose. The peak at 1728 to 1743 cm^{-1} indicates the C=O stretching of the carbonyl ester bond (Reddy *et al*. 2012). The peak of C=O stretching of CA was found at 1732 cm^{-1}. The peak of 1635 to 1651 cm^{-1} indicates the adsorbed water band.

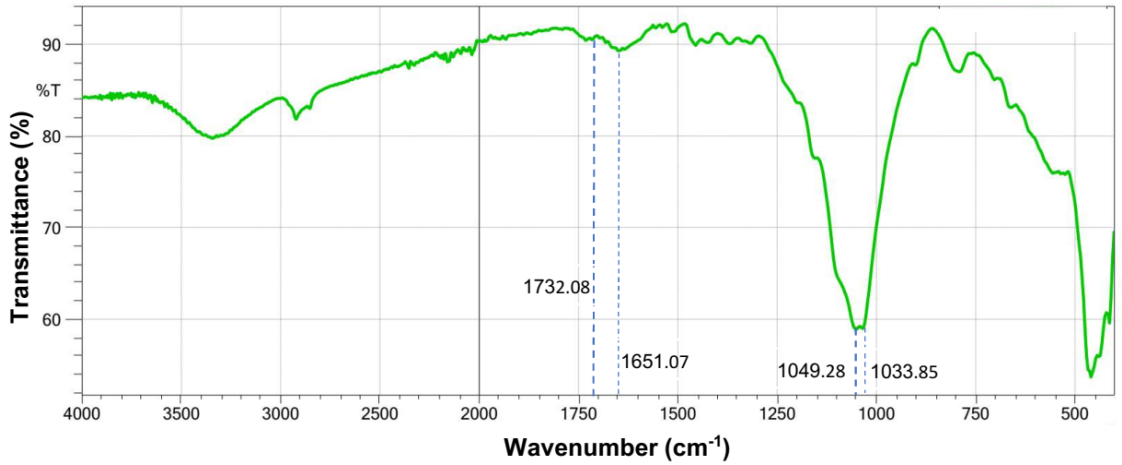

Fig. 9. FTIR spectra of cellulose acetate

The peak height ratio of the carbonyl functional group to the adsorbed water band (1735/1651) shows the substitution degree of acetylation (Maryana *et al*. 2020). Table 4 shows the value of the intensity of peaks at 1735 and 1651 cm^{-1} based on FTIR analysis. Table 4 indicates that the degree of substitution was 1.01.

Table 4. The intensity of Peak of FTIR Analysis

Peak (cm^{-1})	Intensity (a.u)	Ratio
1735	90.41	1.01
1651	89.26	

Figure 10 shows the morphology of CA obtained from rice husk. Figure 10 shows the similarity with the CA obtained from recycled writing papers (Hindi and Abohassan 2015). The two images show a large similarity even though from different raw materials.

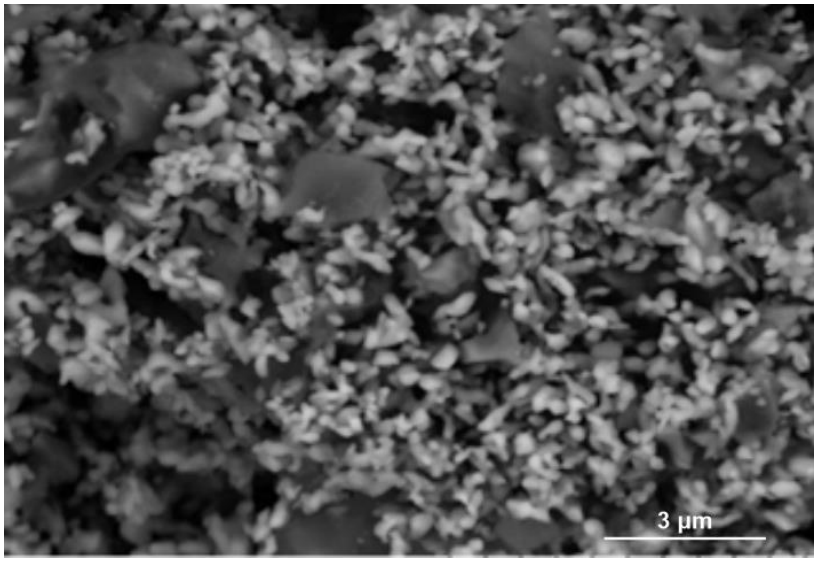

Fig. 10. Morphology of cellulose acetate from rice husk cellulose

CONCLUSIONS

1. Ultrasound-assisted acetylation of rice husk cellulose was successfully carried out. The acetylation process with an iodine catalyst using an ultrasound-assisted process was more effective than the conventional acetylation process (using glacial acetic acid activation and sulfuric acid as a catalyst).
2. The optimum yield of cellulose acetate obtained was 120%, and the process condition for maximum yield was a temperature of 60 °C, a reaction time of 50 min, and a catalyst weight of 10% of cellulose weight.
3. The characteristics of Fourier transfor infrared (FTIR) spectrum and morphology of the cellulose acetate obtained were similar to those of cellulose acetate from other cellulose sources and the value DS of 1.01.

ACKNOWLEDGEMENTS

This work was supported and partially by Majelis Pendidikan Tinggi Penelitian dan Pengembangan Pimpinan Pusat Muhammadiyah with contract number: 0842.262/ PT/I.3/C/2021.

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Article submitted: January 10, 2023; Peer review completed: February 4, 2023; Revised version received: February 9, 2023; Accepted: May 3, 2023; Published: May 18, 2023.
DOI: 10.15376/biores.18.3.4688-4698