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Synthesis of Methyl Cellulose from Rice Husk Cellulose (*Oryza sativa L.*) with Methylene Chloride Through Etherification Reaction

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ABSTRACT

Methyl cellulose is synthesized by an etherification reaction between α-cellulose created by isolating rice husks (*Oryza sativa L.*) with methylene chloride. Methylcellulose synthesis is performed by combining 1 g α-cellulose with acetone solvents at variations of methylene chloride 6 g, 8 g, 10 g, 12 g, and 14 g for 6 hours, resulting in 0.47 g, 0.60 g, 0.58 g; 0.51 g; and 0.69 g of methylcellulose. The results of methyl cellulose synthesis were tested with Degrees of Substitution, FT-IR spectroscopic analysis, and surface morphology using SEM. In the variation of methylene chloride, methylcellulose has the highest degree of replacement (14 g of 01,17). The formation of methyl cellulose is supported by FT-IR spectroscopy, namely with the appearance of vibration peaks in the wave number area of 3295.0 $cm^{-1,}$ which shows the -OH group, the C-H stretching group at wave number 2892.4 cm-1, the absorption peak that indicates the presence of C-O-C is found in wave numbers 1152.6 cm^{-1} and 1021.3 cm^{-1} where it is an asymmetrical and symmetrical stretching vibration. Morphological analysis using SEM showed that cellulose fibers' surface is smoother than methylcellulose. The average size of cellulose and methyl cellulose fibers is 4.791 μm and 3.828 μm, respectively. Morphological analysis using SEM showed that the surface fibers in cellulose were smoother than methylcellulose. The average size of cellulose and methyl cellulose fibers was 4.791 μm and 3.828 μm.

Keywords: Cellulose, Etherification Methyl Cellulose, Methylene Chloride

ABSTRAK

Metil selulosa telah disintesis melalui reaksi eterifikasi antara α-selulosa hasil isolasi dari sekam padi (*Oryza sativa* L.) dengan metilen klorida. Sintesis metil selulosa dilakukan dengan cara merefluks 1 g α-selulosa dengan pelarut aseton pada variasi metilen klorida 6 g, 8 g, 10 g, 12 g, dan 14 g selama 6 jam menghasilkan 0,47 g; 0,60 g; 0,58 g; 0,51 g; dan 0,69 g metil selulosa. Hasil sintesis metil selulosa diuji dengan Derajat Substitusi, analisis spektroskopi FT-IR dan morfologi permukaan menggunakan SEM. Dimana metil selulosa yang memiliki derajat substitusi tertinggi pada variasi metilen klorida 14 g sebesar 1,17. Terbentuknya metil selulosa didukung oleh spektroskopi FT-IR yaitu dengan munculnya puncak vibrasi pada daerah bilangan gelombang 3295,0 cm^{-1} yang menunjukkan gugus -OH, gugus C-H stretching pada bilangan gelombang 2892,4 cm^{-1}, puncak serapan yang menunjukkan adanya C-O-C ditemukan pada bilangan gelombang 1152,6 cm^{-1} dan 1021,3 cm^{-1} dimana masing-masing merupakan vibrasi stretching asymetrical dan symmetrical. Hasil analisis morfologi menggunakan SEM menunjukkan bahwa permukaan serat pada selulosayang lebih halus dibandingkan metil selulosa, rata-rata ukuran serat selulosa dan metil selulosa masing-masing adalah 4,791 μm dan 3,828 μm.

Keyword: Metil Selulosa, Selulosa, Metilen Klorida, Eterifikasi

1. Introduction

Rice is the most widely cultivated food crop in Indonesia. Indonesia. Rice is cultivated to produce rice and is the most widely consumed food. However, rice processing into rice has residual waste in the form of husks. The more rice production, the more rice production, the more husk waste is produced. Chaff is part of the grain of (cereals) in the form of sheets that are dry, scaly, and inedible, which protects the inside (Endospermium and embryo) [1]

Rice husk is one of the residues from rice processing that needs to be handled further or reutilized, handled further or reutilized, which is 45%-50%. The composition indicates the high cellulose content of the husk. Rice husk is a material that contains lignocellulose like other biomass and silica. Other biomass also contains high silica content. The chemical content of rice husk consists of 45-50% cellulose, 25-30% lignin, and 15-20% silica. Rice husk waste is said to be a by-product of the rice milling process. The amount is about 25% of the initial weight of the grain, causing its production to increase and accumulate in the environment [2]

The cellulose content of rice husk is quite high, about 58.852% [3].Rice husk waste is mostly used as an alternative during the dry season, and the rest is burned, causing new environmental problems, such as increasing air pollution, which is bad for human health, can harm human health, and can damage the earth. Therefore, it is necessary to maximize the utilization of rice husk waste that can be profitable and not harmful to the environmental benefit and not damage the environment.

Cellulose is the main component of the cell wall. Cellulose is a polysaccharide consisting of glucose units bonded with β-1,4 glycosidic bond with the formula $(C_6H_{10}O_5)n$, where n is the degree of polymerization. This chemical structure makes cellulose crystalline and insoluble, so it is not easily degraded chemically/mechanically. Glucose molecules are joined into large, long, and chain-shaped molecules to become cellulose. The longer a cellulose chain is, the stronger the cellulose chain has stronger fibers [4].

Studies on plant cellulose fibers have been carried out extensively because of their natural and environmentally friendly nature, easy process, low cost, low energy consumption, lightweight, good specific strength, non-hazardous, and renewable, which is generating interest among researchers than hazardous, renewable which is generating interest among researchers in comparison with conventional synthetic fibers [5]. Researchers use the basic properties of cellulose chemistry to increase its helpful value, which has a reactive surface of hydroxyl groups [6].

There are several cellulose modifications, such as etherification [7], esterification [8], and acetylation [9]. Currently, cellulose has become a material that is widely used in various applications. Cellulose can be chemically modified to create a wider range of derivatives that are used in the industrial sector, which are used in the industrial sector. Today, cellulose has become a material that is widely used in various applications. This is directly related to the paper industry, where cellulose is conventionally processed, such as paper and cardboard. However, although paper and cardboard are the main products of cellulose, it does not necessarily limit the use of cellulose for other uses. These derivatives are further used as agents for coating, laminating, optical films, and adsorbents. In addition, cellulose derivatives can also be found as additives in building materials, pharmaceuticals, food, and cosmetic products

Rahmidar (2018) has modified cellulose into methyl cellulose from pineapple stump and peel with methylene chloride at a ratio of 1:10 using distilled water and acetone solvent at a ratio of 1:20, where the reflux time was 6 hours. This study explained that in methyl cellulose, acetone has a smaller OH/CH ratio value from pineapple bark and peel, so acetone is more efficient to be used as a solvent at the methylation stage [10].

Wahyuningtyas (2021) has researched the Synthesis Optimization of Methyl Cellulose (MC) from Salak Seeds (Salacca edulis Reinw) Pondoh Super. Where, in the alkalization process using 20 mL NaOH with concentration variations of 10, 15, 20, 25, and 30% for 1 hour, the methylation process uses five variations of the use of dimethyl sulfate (2, 3, 4, 5 and 6 mL) as a substitution agent with temperature variations of 45, 50, 55, 60, and 65°C for 180 minutes. This study aims to determine the optimization of methyl cellulose synthesis on NaOH concentration, dimethyl sulfate, and temperature [11].

Based on the description above, researchers are interested in synthesizing methyl cellulose from rice husk cellulose (*Oryza sativa L.)* with methylene chloride 6 g, 8 g, 10 g, 12 g, and 14 g through etherification reaction, and 14 g through etherification reaction using acetone solvent. Characterization of the degree of substitution using Fourier Transform Infra-Red (FTIR) spectroscopy analysis surface morphology test using Scanning Electron Microscopy (SEM), and surface morphology test using Scanning Electron Microscope (SEM).

2. Materials and Methods

2.1. Equipment

The tools used in this study included FT-IR spectroscopy, Scanning Electron Microscopy, triple neck flask, condenser, magnetic bar thermometer, hotplate stirrer, dropper funnel, stative and clamps, desiccator, analytical balance, oven, universal pH indicator, measuring flask, beaker glass, measuring cup, Erlenmeyer cup, porcelain cup, plain filter paper, glass funnel, drip pipette, stirring rod, spatula, gauze filter, plastics and rubber.

2.2. Materials

The materials used in this study were rice husk, methylene chloride, acetone, nitric acid, sodium hydroxide, hydrogen peroxide, sodium hypochlorite, glacial acetic acid, sodium nitrite, and distilled water.

2.3. Sample Preparation

The rice husk is cleaned with water and then dried. After drying, it was weighed using an analytical balance.

2.4. α-Cellulose Isolation

75 g of rice husk was heated with 1 L of a mix of 3.5% HNO_3 and 10 mg $NaNO_2$ at 90°C for 2 hours, then washed until neutral. The residue was heated with 1 L of 2% NaOH solution at 80°C for 4 hours, then washed to neutral. Removal of lignin by heating the residue with 1 L of a solution made of acetate buffer and 1.7% NaOCl in a ratio of 1 1 (v/v). 1: 1 (v/v) ratio at 80°C for 6 hours, then washed until neutral. Then, the hemicellulose was removed by heating the residue with 500 mL of 17.5% NaOH at 80°C for 6 hours. mL of 17.5% NaOH at 80°C for 30 minutes, then washed until neutral. The residue was bleached with 500 mL of 10% H_2O_2 solution at 60°C for 15 minutes and then washed until neutral. The residue was dried at 60°C for 6 hours, then weighed. The results obtained were characterized using FTIR and SEM.

2.5. Synthesis of Methyl Cellulose

1 g of cellulose was soaked with 20 mL of 50% NaOH and stirred using a magnetic stirrer for 24 hours. using a magnetic stirrer for 24 hours, then filtered. The residue was added with 20 mL of acetone and 10 g of methylene chloride. Then, refluxed for 6 hours. Then, the mixture was neutralized with 10% acetic acid and filtered. The residue was washed with warm distilled water. The resulting methyl cellulose was then dried at 50°C for 6 hours. The results obtained were characterized with FT-IR, DS, and SEM. The same procedure was carried out on 6 g, 8 g, 12 g, and 14 g refluxed methylene chloride for 6 hours.

2.6. Determination of the Degree of Substitution

Determination of the degree of substitution of the resulting methyl cellulose was analyzed based on the FT-IR spectrum. The %T intensity values at wave number 1152.6 cm^{-1} (C-O-C group) and 3295.0 cm^{-1} (-OH group) were 84.24 and 87.16, respectively, based on the best variation of 14 g methylene chloride. The degree of substitution value can be calculated based on the equation below.

$$DS = \left[\left(\frac{A1152.6}{A3295.0}\right) - 0.10\right]$$

3. Results and Discussion

3.1 *Isolation of α-cellulose from Rice Husk (Oryza sativa L.)*

α-cellulose was isolated from the rice husk with hydrolysis stage using HNO_3 3.5% to remove hemicellulose and other extractive. The second stage was the delignification using NaOH 2% because it could damage the lignin structure and cause the α-cellulose structure to collapse. Further bleaching uses a mixture of acetate and NaOCl buffer to dissolve the remaining lignin because it degrades into short-chain lignin, easily soluble when washed. Subsequently, the removal of β-cellulose and γ-cellulose is carried out by dissolving the residues in NaOH 17.5% because only α-cellulose is insoluble in this solution. So, the obtained α-cellulose is subdued first using H_2O_2 10%. This bleaching was performed because α- the cellulose obtained was yellowish-white, as shown in Figure 1.

Figure 1. Result of isolated α-cellulose

3.2. *Synthesis of Methyl Cellulose from α-cellulose Isolated from Rice Husk*

Methyl cellulose was synthesized from α-cellulose that was conducted etherization reaction between the α-cellulose with methylene chloride with variations of 6 g, 8 g, 10 g, 12 g, and 14 g and refluxed for 6 hours. The methyl cellulose obtained is shown in Figure 2.

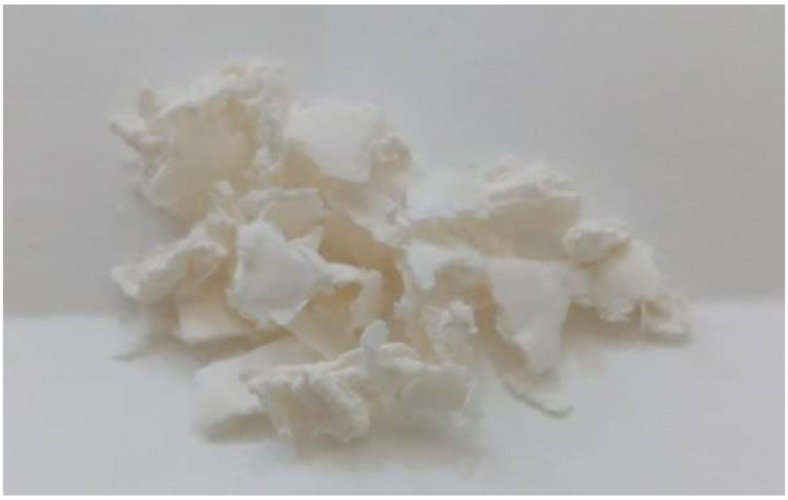


Figure 2. Methyl cellulose result from α-cellulose

3.3. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis from α-Cellulose and Methyl Cellulose Isolated From Rice Husk

In this study, the FTIR analysis results of α-cellulose and methyl cellulose are shown in Figure 3. The cellulose resulting from the insulation of the rice husk has the characteristics of absorption peak at the number of waves 3302.4; 2892.4, 1640; 1416.4, 1371.7, 1325,3; 1158.4, 1021.3; and 885.8 cm^{-1}, each showing the presence of function groups -OH, C-H, (CH_2, CH_3), H-O-H, C-H, C–H, (CH_2), C-H (CH_3), C–O-C, C–O-C, and C–H at of β-glucoside bonding. This corresponds to the characteristics of α-cellulose in previous studies [12-13]. Thus, the isolation of α-cellulose from the plasma has been successfully carried out. Moreover, the main difference between cellulose and methyl cellulase can be observed from a decrease in absorption intensity at a wavelength of approximately 3300-3400 cm^{-1}, which can be attributed to the presence of stretching -OH on the cellulose molecule due to partial replacement of the hydrogen cluster during the matching reaction. In addition, the increase in the intensity of the wavelengths of about 2900-2800 cm^{-1} is due to the stretching of C-H, i.e., of CH and CH_2 of cellulose and CH_3 of methylcellulose [14]. The FT-IR methyl cellulose spectrum typically shows absorption tapes at 1416, 1371, 1325, and 1158 cm^{-1} caused by C-H vibrations of the CH_2 and CH_3 clusters [13-15]

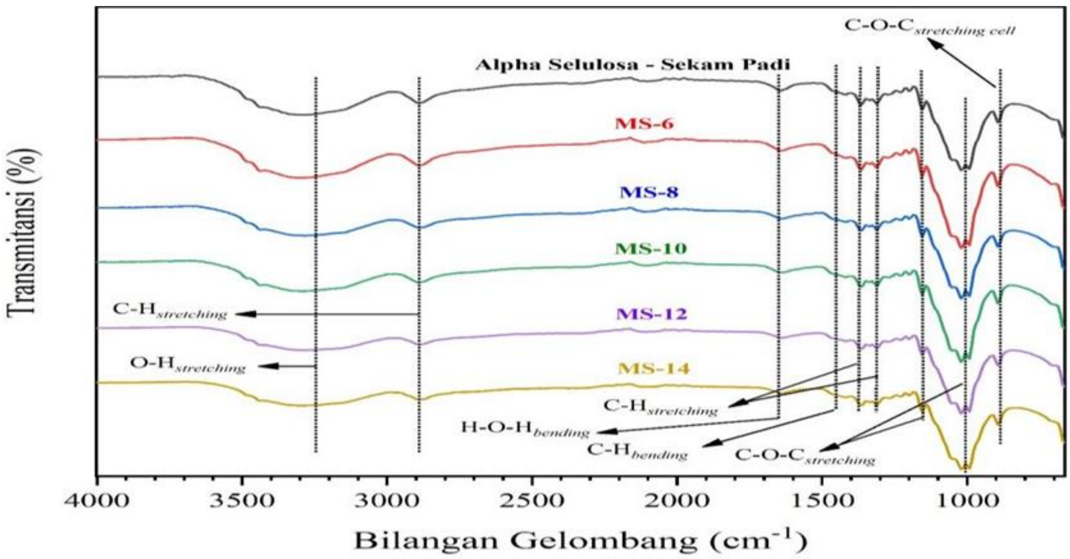


Figure 3. FTIR spectra of α-cellulose and methyl cellulose with methylene chloride variation

Based on Figure 3, it can be seen that cellulase and methyl cellulose have several absorption peaks in the area of the same number of waves. It can be assumed that both samples have structural similarities related to the degree of regularity (crystallinity characteristics), especially in the 1500-1000 cm^{-1} wavelength area where vibrations are associated with the degree of regularity of cellulose-based materials [16]. Furthermore, it can also be observed that the -OH group in cellulose is replaced by the $-CH_3$ group so that -OH groups in methylcellulose decrease their intensity while the peak intensity of C-H absorption increases [10-16]. The change in the absorption tape -OH and C-H is a characteristic that indicates the efficiency of the methylation process. Thus, the synthesis of cellulose-methyl has been successfully carried out. The difference in FTIR spectra of α-cellulose and methyl cellulose is shown in Table 1.

Table 1. The difference in FTIR spectra of α-cellulose and methyl cellulose

Wavenumber (cm^{-1})		Functional Group
α-Cellulose	Methyl Cellulose	
3302.4	3317-3280	-OH
2892.4	2892.4	C-H (CH_2 dan CH_3)
1640.0	1640.0	H-O-H
1416.4	1418.2	C-H (CH_2)
1371.7	1371.7	C-H
1325.3	1325.3	C-H
1158.4	1158.4	C-O-C
1021.3	1021.3	C-O
885.8	885.8	C-H (β-glycoside of cellulose)

The decreasing intensity of the -OH group absorption tape also proves that the greater the likelihood that -OH will be substituted, with methyl cellulose with a variation of 14 g of methylene chloride having the highest degree of substituting among the comparisons of other Methylene Chloride. Cellulose is a polymer with the chemical formula $(C_6H_{10}O_5)n$. In this case, n is the number of repetitions of sugar units or degrees of polymerization whose price varies depending on the source of cellulose and the treatment it receives [17].

3.4. Determination of the Degree of Substitution

Determination of the degree of substitution of methyl cellulose based on the FT-IR spectra can be seen in Table 2.

Table 2. Degree of substitution of methyl cellulose

Methylene Chloride (g)	DS
6	0.86
8	0.93
10	1.02
12	1.09
14	1.17

In this study, the highest DS value was 1.17, derived from methyl cellulose with a variation of 14 g of methylene chloride. Here's the calculation of the substitution degrees that can be calculated based on the following equation: Absorption at the number of waves 1152.6 cm^{-1} (A1152.6)/

%T = 84.24
T = 0.842
A $= \log \frac{1}{0.842}$
A = 0.075

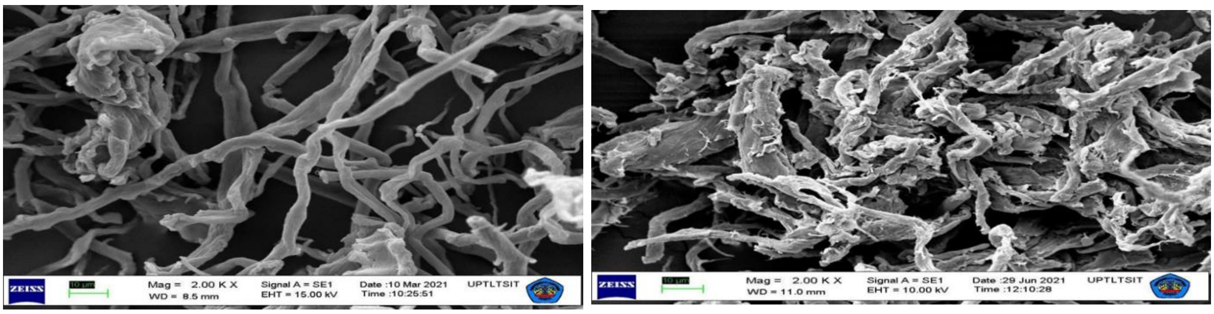
The absorption at the wavenumber 3295.0 cm^{-1} (A3295.0)

%T = 87.16
T = 0.871
A $= \log \frac{1}{0.871}$
A = 0.059

$$DS = \left[\left(\frac{A1152.6}{A3295.0}\right) - 0.10\right]$$
$$DS = \left[\left(\frac{0.075}{0.059}\right) - 0.10\right]$$
$$DS = 1.27 - 0.10$$
$$DS = 1.17$$

3.5. Surface Morphology Analysis Using Scanning Electron Microscopy (SEM) on α-Cellulose and Methyl Cellulose

SEM analysis was performed to look at the surface morphology of the cellulose-modified compounds obtained. These results will show a picture of how well the reagents are interacting in cellulose modification. In this study, the SEM test was carried out by passing the cellulose resulting from a paddle stain with a 2000-fold magnification.



a) **b)**

Figure 4. Morphology SEM of a). α-cellulose from rice husk and b). methyl cellulose

Figure 4 shows the morphology observed that the cellulose fiber surface has a more fine fiber surface than the methyl cellulose. It can be assumed that a change in the function group of cellulose substituted by CH_3 can affect the morphology of cellulosic fibers. Based on the calculation of the fiber size using the ImageJ application, it is found that the average size of cellulose fibers and methyl cellulose is 4.791 μm and 3.828 μm, respectively. (Figure 4.b). It also explains that cellulose modified by replacing the -OH group with the CH_3 group can decrease the size of the cellulose fiber.

4. Conclusion

Methyl cellulose is the result of synthesis between α-cellulose and methylene chloride. A total of 1 g of α-cellulose was synthesized with 6 g, 8 g, 10 g, 12 g, and 14 g of each of the methylene chlorides, resulting in 0.47 g, 0.60 g, 0.58 g; 0,51 g, and 0.69 g of methylene cellulose. Next, methyl cellulose is characterized based on analysis of FT-IR, Degree of Substitution, and SEM. Methyl Cellulose has the highest degree of substitution in the 14 g Methylene Chloride variation of 1.17. The formation of methyl cellulose is supported by FT-IR spectroscopy, i.e., by the appearance of peak vibrations in the range of wavelengths of 3295,0 cm-1 showing the group -OH, the group C-H stretching at the number of waves of 2892,4 cm-1, the absorption point showing C-O-C being found at the wave numbers of 1152,6 cm-1 and 1021,3 cm-1 where each is an asymmetric and symmetrical stretching vibration. Based on surface survey results showing that cellulose fiber surfaces have a more fine fiber surface compared to methylcellulose, the average size of cellulase fiber and methyl cellulose fiber are 4,791 μm and 3,828 μm, respectively.

5. Acknowledgements

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6. Conflict of Interest

Authors declare no conflicts of interest.

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