Vol.7, No.2, 2022
e-ISSN 2502-4787

THERMAL STABILITY ANALYSIS OF CELLULOSE FROM SAGO FIBER WASTE (*Metroxylon sago)*

Nurmalasari[1], Sastriana Jaya Lestari[1], Mimi Syamsuddin[1], Sukarti[1], Muhammad Nur Alam[1]

[1]*Universitas Cokroaminoto Palopo, Faculty of Science, Jl. Latamacelling No.19 Palopo 91921, South Sulawesi, Indonesia*

E-mail: *nur87.mipa@gmail.com

Received: 17 Desember 2021. Accepted: 19 November 2022. Published: 31 Desember 2022

DOI: 10.30870/educhemia.v7i2.13491

Abstract: Sago pulp is a lignocellulosic waste rich in cellulose, so that it can be used optimally as a source of carbon and cellulose. Fixed carbon can be obtained maximally by determining the carbonization temperature. This research aims to determine the temperature of the cellulose sample starting to decompose and the energy required at the time of decomposition. The process of extracting cellulose from sago fiber waste uses NaOH alkalinization for delignification, bleaching with H2O2, and hydrolysis with HCl. Identification of lignin in sago fiber is known by the appearance of the C=O group in the wave region of 1734.01 cm-1 with strong intensity; after extraction, no peak number was found in the extracted cellulose FTIR spectrum. TGA analysis of cellulose underwent two stages of mass change, the first stage of decomposition of water molecules at a temperature of 47°C-203°C obtained a mass decrease of 5.69%, and the second stage of decomposition at a temperature of 287°C-397°C obtained a mass decrease of 58.95%. DSC analysis obtained two thermal properties of physical changes contained in two endothermic peaks, the first peak of water evaporation which required energy of 28,1120 J/g, and the second peak of decomposition, which required energy of 9.6188 J/g.

Keywords: Cellulose; Extraction; FTIR; TGA; DSC

Abstrak: Ampas sagu merupakan limbah lignoselulosa yang kaya akan selulosa sehingga dapat dimanfaatkan secara optimal sebagai sumber karbon dan selulosa. Penelitian ini bertujuan untuk mengetahui temperatur sampel selulosa yang mulai terdekomposisi dan energi yang dibutuhkan pada saat dekomposisi. Proses ekstraksi selulosa dari limbah serat sagu menggunakan alkalinisasi NaOH untuk delignifikasi, pemutihan dengan H_2O_2, dan hidrolisis dengan HCl. Identifikasi lignin pada serat sagu diketahui dengan munculnya gugus C=O pada daerah gelombang 1734,01 cm^{-1} dengan intensitas kuat, setelah ekstraksi tidak ditemukan bilangan puncak pada spektrum FTIR selulosa yang diekstraksi. Pada analisis TGA, selulosa mengalami dua tahap perubahan massa. Tahap pertama pelesapasan molekul air pada suhu 47°C-203°C diperoleh penurunan massa sebesar 5,69%, dan tahap kedua penguraian pada suhu 287° C -397°C didapatkan penurunan massa sebesar 58,95%. Analisis DSC diperoleh dua sifat termal perubahan fisis yang terdapat pada dua puncak endotermik, puncak pertama penguapan air yang membutuhkan energi sebesar 28,1120 J/g, dan puncak kedua dekomposisi yang membutuhkan energi sebesar 9,6188 J/g.

Kata kunci: Selulosa; Ekstraksi; FTIR; TGA; DSC.

INTRODUCTION

Sago (Metroxylon sago) is a plant that is widely distributed in Indonesia, and belongs to the monocotyledonous plant of the Metroxylon plantae family with the order Spadicifflorae. Sago has a higher starch content than other types of Metroxylon, so sago is widely used in various agricultural industries (Amin et al., 2019). Currently, the use of sago is still focused on the starch contained in it (Ernawati et al., 2018). In the sago production process, three types of waste are generated, namely fibrous sago pith waste (sago pulp), sago bark (bark) and waste water (waste water) (Ngaini et al., 2018, 2014; Wahi et al., 2017). The sago bark and sago pulp produced from the sago production process are about 26% and 14%, respectively, based on the total weight of the sago stalks.

Sago pulp is a product obtained from the extraction process of sago starch. It often become waste which is quite a lot and is rarely processed for use. If left unchecked sago pulp can cause environmental pollution in the form of odor and trigger an increase in soil acidity. Sago waste in the form of sago pulp contains about 58.21% starch and the rest is in the form of crude fiber, crude protein, fat, and ash. Sago pulp waste is a lignocellulosic waste that is rich in cellulose, so it can be used optimally as a carbon source (Lim, 2006).

Carbon from sago pulp has an ash content that does not meet SNI (Mulyasari et al., 2020). To overcome this deficiency, it is necessary to extract cellulose from sago pulp. Cellulose can be obtained from bark, midrib, sago leaves and sago pulp (Naduparambath et al., 2018; Quan et al., 2016; Tabugon et al., 2021; Veeramachineni et al., 2016).

The thermal stability of cellulose from plants has been extensively studied. Several studies found related to the thermal stability of cellulose from plants of the Arecaceae family have been reported (Alothman et al., 2021; Foadieng et al., 2017; Lamaming et al., 2015; Madhu et al., 2019; Poletto et al., 2014), but the thermal properties of cellulose from sago fiber waste have not been found. Although several studies on the thermal stability of cellulose have been reported, there have not been many studies on the thermal properties of cellulose from sago fiber waste. This paper mainly reports the results of research on the thermal properties of sago and its content. Thermal characterization

is performed using DTG and DSC measurements which allow investigation of events and damage at high temperatures. Another observation has also been made, which is the observation of functional groups of materials using FTIR.

METHOD

Research Method

This research instrument consisted of: oven, analytical balance, measuring cup, beaker, pH parameter, glass funnel, stirring rod, spatula, 60 mesh sieve, desiccator, measuring flask. While the analytical tools used are SHIMADZU FTIR (Fourier Transform Infrared) Spectroscopy, Thermal Gravimetric Analysis (TGA) Platinum LINSEIS STA series (simultaneous thermal analysis), and Perkin Elmer's Differential Scanning Calorimetry (DSC).

The material used in this study is sago fiber from Benteng Village, Malangke District, North Luwu Regency. The chemicals used are sodium hydroxide (NaOH) solution, hydrogen peroxide (H_2O_2) solvent, hydrochloric acid (HCl) solution. As well as other materials, namely aquadest, tissue, aluminum foil and filter paper.

Research Procedure

Sago pulp preparation

The first step is to wash the sago fiber with water to remove impurities, then dry it in direct sunlight for 3 days. Then cooled in a desiccator and weighed to a constant weight. After that, the dried sago fiber is then blended and filtered using a sieve.

Extraction of Cellulose from Sago Fiber Waste

Sago fiber waste was weighed as much as 10 grams, then added 120 mL of 1M NaOH solution and refluxed for 1 hour 36 minutes at 80 °C. After that, the refluxed sago fiber waste was filtered and washed until the filtrate was clear, then continued with the bleaching process using 140 ml H_2O_2 solution for 18 minutes at 80°C. After that, the sago fiber was filtered again and washed until the filtrate was clear. Furthermore, the clear sago fiber was hydrolyzed with 65 ml of 2N HCl, stirring with a magnetic stirrer for 30 minutes at room temperature. After that, the sago fiber was then filtered and washed with the pH of the filtrate reaching 7. Then it was dried using an oven for 24 hours at 50 °C, then stored in a dry place before being analyzed.

Cellulose Characterization

FTIR Analysis

KBr was ground up to <200 mesh and dried in an oven at 120°C for 24 hours, then stored in a desiccator containing a drying agent. About 1-2 mg of sample and mixed with 200 mg of KBr powder until evenly distributed in a mortar, make a pellet sample. The KBr pellet was taken using tweezers and placed on the provided frame. Place the frame on the spectrophotometer, then it is analyzed and the spectrum is taken. Perform the previous step using a single KBr powder. Identify the functional groups (wave numbers) of the sample's infrared spectrum using a correlation table.

TGA-DSC Thermal Analysis

The 0.3 gram cellulose sample was placed in a pan, then closed using stainless steel using a crimp tool. Place the comparison sample on the plate glass. Measurements were made from a temperature of 20°C - 500°C with a temperature increase of 10°/min, with nitrogen gas (N_2) flowing.

RESULTS AND DISCUSSION

Based on the research that has been carried out, the results obtained from the extraction of cellulose from sago fiber waste as shown in Figure 1that Showing the color of the sample in the form of brown, after going through the extraction process the sample becomes white in the form of a thin sheet with a small size.

(a) (b)

Figure1. Sampel (a) Sago Fiber, (b) Cellulose Extraction Results

In this research, the extraction process of cellulose from sago fiber waste was carried out through three extraction stages, namely delignification, bleaching, and hydrolysis. Sago fiber samples were given extraction treatment where the initial treatment was delignification with NaOH to remove lignin and hemicellulose, followed by a bleaching process with H_2O_2 to remove residual lignin after delignification (Nguyen et al., 2022), then hydrolysis using HCl to obtain cellulose. From the results obtained as much as 1.64 grams of cellulose, with the randomness of cellulose obtained from the extraction process of 4.1%.

Cellulose Characterization Results

FTIR

The results of the characterization of cellulose extraction from sago fiber waste

using FTIR were carried out to determine the functional groups in the extraction results and sago fiber.

The FTIR spectrum is extracted from cellulose and the original material is sago fiber waste. The results of the spectrum analysis of the extracted cellulose and the resulting sago fiber can be seen in Figure 2 and Table 1.

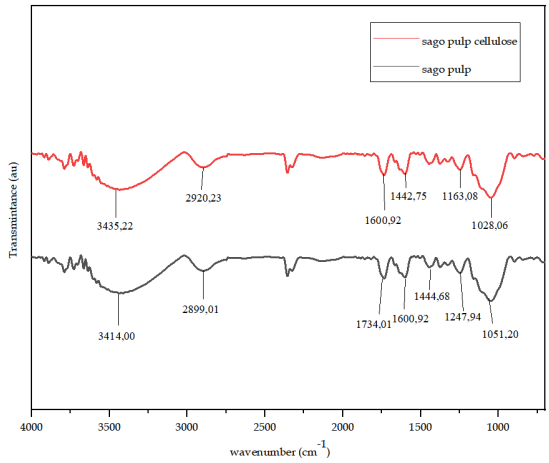

Figure 2. FTIR spectrum of sago and fiber

Table 1. Wave Number of Sago Fiber and Cellulose

Wave Number (cm-1) and Intensity		Functional Group
Sago Fiber	**Cellulose**	
3414.00 (s,b)	3435.22 (s,b)	O-H
2899.01 (m)	2920.23 (m)	C-H Alifatik
1734.01 (s, *sharp*)	Not Found	C=O
1600.92 (s, *sharp*)	1600.92 (m)	C=C
1444.68 (m)	1442.75 (m)	CH_2
1247.94 (m)	1163.08 (w)	C-O
1051.20 (s)	1028.06 (m)	C-O-C

The delignification, bleaching and hydrolysis treatment of sago fiber in the cellulose extraction process resulted in reduced lignin as indicated by the reduced intensity of the absorption band in the extracted cellulose spectra in the area of 1600.92 cm^{-1} (C=C) and 1051.20 cm^{-1} (C-O-C).

This treatment was also effective in removing hemicellulose compounds which were indicated by the absence of peaks or absorption bands in the area of 1728.22 cm^{-1} which previously had a fairly high intensity in the spectra of sago fiber.

The FTIR spectra of the extracted cellulose showed the absorption of the stretching O-H group in the area of 3435.22 cm^{-1}(Biswas et al., 2017; Kinney et al., 2012). Absorption of aliphatic C-H groups from cellulose was also identified at wave number 2920.23 cm^{-1}. The C-H functional group is a cellulose skeleton that appears in the wave number range of 2800-3000 cm^{-1} where this group is located to the right of the O-H group. In the absorption area of 2900 cm^{-1}, there is C-H stretching on CH_2 from the CH_2-OH group (Naduparambath et al., 2018). The C-O group as a constituent of the cellulose structure is also read in the ir-spectrum of cellulose shown in the 1163.08 cm^{-1} region. With the identification of functional groups O-H, C-H, and C-O at various absorption peaks, thus indicating that the IR

spectrum is cellulose compounds (Pratiwi et al., 2020).

Thermal Analysis

Thermal analysis of cellulose from sago fiber waste produced was obtained through characterization using TGA and DSC instruments. The TGA themogram provides information on the decrease in mass with respect to temperature and the DTG themogram is a derivative of the TGA which shows the rate of mass loss. While the DSC thermogram informs the heat required for the cellulose sample.

Test Result of *Thermal gravimetric analysis* (TGA)

In this research, cellulose from sago fiber was analyzed using TGA (thermal gravimetry analysis) using nitrogen gas, nitrogen was used to prevent premature degradation. Polymer degradation is related to the change in the properties of a polymer due to changes in the bonds in the main or main chain. The DTG (derivative thermogravimetric) themogram is the rate of change of mass, the higher the heating, the sharper the peak of the DTG graph. The higher the heating rate, the higher the decomposed compound. This causes the peak to be sharper. Increased heating can increase the temperature change at each stage, which is caused by heat transfer.

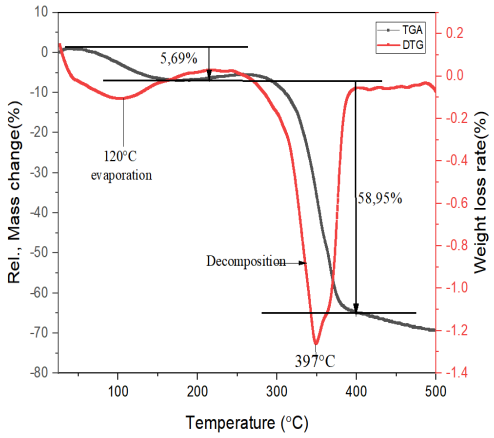

Figure 3. TGA Themogram Curve and DTG Cellulose Sago Fiber

In Figure 3 it can be seen that sago fiber cellulose undergoes two stages of mass reduction. The first stage in the temperature range of 47°C-203°C obtained a mass decrease of 5.69%. The rate of mass loss with a low peak as seen in the DTG curve. In the picture it can be seen that there is decomposition. At this stage the cellulose is dehydrated, where there is evaporation or the decomposition of water molecules during heating. Water loss occurs at a temperature of about 100°C (Poletto et al., 2014).

The second stage in the temperature range of 287°C -397°C obtained a mass reduction of 58.95%. The DTG curve shows that there is a sharp peak. This happens because of the high heating. At an initial temperature of 287°C the decomposition of materials other than carbon such as hemicellulose occurs. The decomposition of materials other than

carbon such as cellulose, hemicellulose, and lignin occurs at temperatures of 200°C-340°C (Joseph et al., 2003; Plis et al., 2016; Poletto et al., 2014; Ufodike et al., 2020; Veeramachineni et al., 2016).

The decomposition process takes place up to a temperature of 397°C where at this temperature the mass is constant in the final stage of heating, so that a complete decomposition occurs and no further mass decrease occurs. Thermal breaking of chemical bonds will form carbon charcoal in the decomposition process (Tabugon et al., 2021). The decomposition of the material is known from the change in sample weight to the formation of charcoal. From the results of the TGA temogram, it can be seen that cellulose has thermal resistance properties up to a temperature of 397°C, so for the carbonization process the right temperature is used, namely a temperature of 287°C -397°C.

Test Result of *Differential Scanning Calorimetry* (DSC)

DSC (Differential Scanning Calorymetry) is a technique used to analyze and measure the difference in heat entering the sample and the reference as a comparison. The themogram of the DSC analysis of a polymeric material will provide information on the decomposition point (Td), which is when the polymer begins to break down or degrade (Cichosz and Masek, 2019; Jandura et al., 2000).

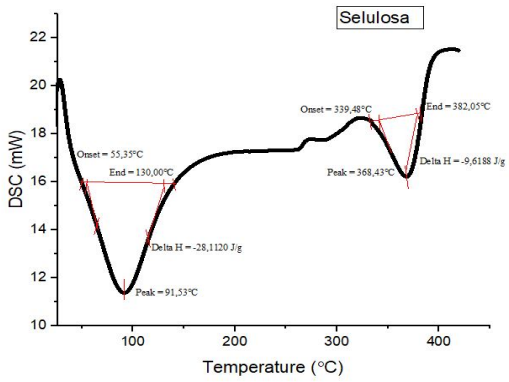

Figure 4. The sago fiber cellulose DSC temogram curve

In this research, cellulose from sago fiber was analyzed using DSC (Differential Scanning Calorymetry) with an initial heating temperature of 25°C-450°C. Figure. 4 it can be seen that the themogram of the sago fiber cellulose sample has undergone evaporation of water content and decomposition due to heating. At a temperature of 55.35°C which is widened to 130°C, the sample undergoes an endothermic reaction that requires energy as much as -28.1120 J/g showing a thermogram peak, where the endothermic peak is at 91.533◦C. This peak shows physical changes, the loss of water groups that are still present in the extraction results, it is known that water begins to evaporate at a temperature of 100°C. The endothermic peak shows the dehydration profile of the sample, this

dehydration is related to the loss of H_2O from the sample that is physically bound to its surface (Jandura et al., 2000).

Cellulose decomposition occurs at a temperature of 339.48°C which is widened to 382.05°C, the sample undergoes an endothermic reaction that requires energy as much as -9.6188 J/g showing a sharp thermogram peak, where the endothermic peak is at 368.43°C. This peak indicates a physical change, where sago fiber cellulose is heated high enough to decompose so that it will form carbon charcoal.

CONCLUSION

From the results of research that has been carried out regarding the analysis of the thermal resistance of cellulose from sago fiber waste, it can be concluded that cellulose from sago pulp waste can be used as a carbon source. The pyrolysis temperature that can be used is 287°C - 397°C which results in a mass reduction of 58.95%. DSC analysis showed two thermal properties of physical changes which showed two endothermic peaks, where the first peak showed evaporation of water at 55.35°C which expanded to 130°C, where the sample underwent an endothermic reaction which required energy of 28.1120 J/g and endothermic peak at 91.53°C. While the second peak indicates that cellulose begins to decompose which occurs at a temperature of 339.48°C which widens to 382.05°C, where the sample undergoes an endothermic reaction which requires energy of 9.6188 J/g and the themogram peak is at 368.43° C .

REFERENCES

Alothman, O.Y., Kian, L.K., Saba, N., Jawaid, M., Khiari, R., 2021. Cellulose nanocrystal extracted from date palm fibre: Morphological, structural and thermal properties. Ind. Crops Prod. 159, 113075.

Amin, N., Sabli, N., Izhar, S., Yoshida, H., 2019. Sago wastes and its applications. Pertanika J. Sci. Technol. 27, 1841–1862.

Biswas, B., Pandey, N., Bisht, Y., Singh, R., Kumar, J., Bhaskar, T., 2017. Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk. Bioresour. Technol. 237, 57–63.

Cichosz, S., Masek, A., 2019. Cellulose Fibers Hydrophobization via a Hybrid Chemical Modification. Polym. 2019, Vol. 11, Page 1174 11, 1174.

Ernawati, E., Lakare, H., Diansari, P., 2018. Peranan Makanan Tradisional Berbahan Sagu sebagai Alternatif Dalam Pemenuhan Gizi Masyarakat. J. Sos. Ekon. Pertan. 14, 31–40.

Foadieng, E., Talla, P.K., Nkamgang, G.B., Fogue, M., 2017. Study of the Thermal Properties of Raffia Bamboo Vinifera L. Arecaceae. Adv. Mater. Sci. Eng. 2017.

Jandura, P., Riedl, B., Kokta, B. V., 2000. Thermal degradation behavior of cellulose fibers partially esterified with some long chain organic acids. Polym. Degrad. Stab. 3, 387–394.

Joseph, P. V., Joseph, K., Thomas, S., Pillai, C.K.S., Prasad, V.S., Groeninckx, G., Sarkissova, M., 2003. The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Compos. Part A Appl. Sci. Manuf. 34, 253–266.

Kinney, T.J., Masiello, C.A., Dugan, B., Hockaday, W.C., Dean, M.R., Zygourakis, K., Barnes, R.T., 2012. Hydrologic properties of biochars produced at different temperatures. Biomass and Bioenergy 41, 34–43.

Lamaming, J., Hashim, R., Leh, C.P., Sulaiman, O., Sugimoto, T., Nasir, M., 2015. Isolation and characterization of cellulose nanocrystals from parenchyma and vascular bundle of oil palm trunk (Elaeis guineensis). Carbohydr. Polym. 134, 534–540.

Lim, J.K., 2006. Preparation and Characterization of Carboxymethyl Sago Waste and its Hydrogel.

Madhu, P., Sanjay, M.R., Pradeep, S., Subrahmanya Bhat, K., Yogesha, B., Siengchin, S., 2019. Characterization of cellulosic fibre from Phoenix pusilla leaves as potential reinforcement for polymeric composites. J. Mater. Res. Technol. 8, 2597–2604.

Mulyasari, A., Kimia, S., Sains, F., Palopo, U.C., Selatan, S., 2020. Analisis proksimat karbon aktif limbah serat sagu teraktivasi koh 1. Cokroaminoto J. Chem. Sci. 2, 20–22.

Naduparambath, S., T.V., J., Shaniba, V., M.P., S., Balan, A.K., Purushothaman, E., 2018. Isolation and characterisation of cellulose nanocrystals from sago seed shells. Carbohydr. Polym. 180, 13–20.

Ngaini, Z., Noh, F., Wahi, R., 2014. Esterified sago waste for engine oil removal in aqueous environment. http://dx.doi.org/10.1080/09593330.2014.920051 35, 2761–2766.

Ngaini, Z., Noh, F., Wahi, R., 2018. Facile sorbent from esterified cellulosic sago waste for engine oil removal in marine environment. Int. J. Environ. Sci. Technol. 15, 341–348.

Nguyen, P.X.T., Ho, K.H., Do, N.H.N., Nguyen, C.T.X., Nguyen, H.M., Tran, K.A., Le, K.A., Le, P.K., 2022. A comparative study on modification of aerogel-based biosorbents from coconut fibers for treatment of dye- and oil-contaminated water. Mater. Today Sustain. 19, 100175.

Plis, A., Lasek, J.A., Zuwała, J., Yu, C.C., Iluk, A., 2016. Combustion performance evaluation of Posidonia oceanica using TGA and bubbling fluidized-bed combustor (batch reactor). J. Sustain. Min. 15, 181–190.

Poletto, M., Ornaghi Júnior, H.L., Zattera, A.J., 2014. Native Cellulose: Structure, Characterization and Thermal Properties. Mater. (Basel, Switzerland) 7, 6105–6119.

Pratiwi, S.W., Sari, S.N., Nurmalasari, R., Indriani, M., 2020. Utilization of Nata De Coco as Adsorben in Methyl Orange Adsorption. EduChemia (Jurnal Kim. dan Pendidikan) 5, 187.

Quan, C., Gao, N., Song, Q., 2016. Pyrolysis of biomass components in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and product characterization. J. Anal. Appl. Pyrolysis 121, 84–92.

Tabugon, H.C., Oracion, J.P.L., De La Rosa, L.B., Grumo, J.C., Alguno, A.C., Deocaris, C.C., Capangpangan, R.Y., 2021. Synthesis and characterization of cellulose nanocrystals extracted from sago (Methoxylon sagu) pulp. AIP Conf. Proc. 2370, 020022.

Ufodike, C.O., Eze, V.O., Ahmed, M.F., Oluwalowo, A., Park, J.G., Liang, Z., Wang, H., 2020. Investigation of molecular and supramolecular assemblies of cellulose and lignin of lignocellulosic materials by spectroscopy and thermal analysis. Int. J. Biol. Macromol. 146, 916–921.

Veeramachineni, A.K., Sathasivam, T., Muniyandy, S., Janarthanan, P., Langford, S.J., Yan, L.Y., 2016. Optimizing extraction of cellulose and synthesizing pharmaceutical grade carboxymethyl sago cellulose from Malaysian sago pulp. Appl. Sci. 6.

Wahi, R., Chuah Abdullah, L., Nourouzi

Mobarekeh, M., Ngaini, Z., Choong Shean Yaw, T., 2017. Utilization of esterified sago bark fibre waste for removal of oil from palm oil mill effluent. J. Environ. Chem. Eng. 5, 170–177.