

Characteristics of *Metroxylon rumphii* (pith and bark waste) from Seram Island, Maluku, Indonesia

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Abstract. Siruru H, Syafii W, Wistara I. N. J, Pari G. 2019. Characteristics of *Metroxylon rumphii* (pith and bark waste) from Seram Island, Maluku, Indonesia. *Biodiversitas* 20: 3517-3526. Sago (*Metroxylon rumphii* Martius) pith waste (SPW) and sago bark waste (SBW) are lignocellulosic materials that can be used for various needs directly or indirectly. It is necessary to understand SPW and SBW characteristics to maximize their utilization. In this study, we analyzed the proximate, ultimate, and crystallinity by XRD, the functional groups by FTIR, morphology by SEM, and the derivate analysis of hot water-soluble extractives by GCMS. The contents of SPW and SBW hot-water soluble extractive, lignin, and holocellulose were 57.7 and 4.9%, 6.1 and 29.4%, and 45.74 and 66.74%, respectively. The volatile matter, ash content, silica, fixed carbon, C, H, and O contents of the SPW and SBW were 81.48 and 84.56%, 1.30 and 3.04%, 1.25% and 2.03, 12.77 and 18.06%, 37.93 and 44.64%, 6.37 and 6.49%, and 47.75 and 51.10%, respectively. The degree of crystallinity of SPW was 15.04%, while that of SBW was 47.28%, where both have a monoclinic structure with the main peak by 2θ 16° and 26°. SPW and SBW contained several minerals such as silica, boron, sulfur, and phosphorus. The surface morphology of the SPW was porous with a small diameter and thin cell wall, while that of SBW was covered by minerals. Nitrogen, alcohol, and sugar group compounds were found more in SPW, whereas phenol compound was more in SBW. SBW has high lignin content and SPW has a very large amount of hot water-soluble extractive.

Keywords: Boron, hydrazine, *Metroxylon rumphii*, saccharification

INTRODUCTION

Biomass is an organic material that has specific chemical structure and chemical reactivity (Carrier et al. 2011) and generates different products at different temperatures (Gaojin et al. 2012). Biomass can be obtained from various agricultural and forestry wastes such as sago waste (*Metroxylon* sp.). However, biomass has specific properties according to the type, place of growth, and environmental conditions (Park et al. 2017). Therefore, it is necessary to understand biomass properties before it is utilized.

Previous studies have reported the differences in the chemical components of larch type in different growing sites (Grabner et al. 2005) and differences in starch content based on the age of sago plant (Pei-Lang et al. 2006). The structural components of biomass are holocellulose (cellulose + hemicellulose) and lignin (Carrier et al. 2011) while non-structural components are extractive (Nascimento et al. 2013) and inorganic compounds (Sharma et al. 2004). According to Shmulsky et al. (2011), the total percentage of structural and non-structural components is 100%. However, previous studies about the utilization of sago waste conducted by Utami (2018) and Linggang et al. (2012) used starch content to represent non-structural components. On the other hand, Sjoström (1998)

reported that non-structural components contain various compounds. Therefore, study about non-structural components of sago waste is an interesting topic.

Sago (*Metroxylon* sp.), a plant producing sago flour, is considered as an economically valuable crop in several countries such as Malaysia, Indonesia, Philippines, and New Guinea (Ehara et al. 2018). There are several residents in Indonesia, i.e., Irian, Maluku, Aceh and the Mentawai islands in West Sumatra consuming sago flour as a source of carbohydrates (Bintoro et al. 2010). Processing of sago stems produces approximately 25% sago flour and about 75% waste (McClatchey et al. 2006). This huge amount of waste has good potential to be utilized since only a few portions of this waste is used as an ameliorant material (Zaimah et al. 2012) and animal feed (Phang et al. 2000), while the rest is left unused and causes environmental problem (Awg-Adeni et al. 2013). Therefore, to increase the value-added of sago waste, it is necessary to analyze the sago waste. By knowing the characteristics of sago waste, it can be determined which products will be produced from the potential raw material of the sago waste. SPW is sago pith waste in which the starch has been extracted (Lai et al. 2013; Yacob et al. 2018). SPW is dominated by parenchyma cells. Meanwhile, SBW is the outer part of a stricter sago stem (Wahi et al. 2017) or peripheral parts which are dominated by sclereid cells. The

purpose of this study was to analyze the characteristics of sago waste, i.e., sago pith waste (SPW) and sago bark waste (SBW).

MATERIALS AND METHODS

Materials

The research was conducted from October to December 2018. *Metroxylon rumphii* was used sago sample. SPW and SBW were obtained from traditional sago flour processing farmers in Amahai Village, Central Maluku Regency, Indonesia. SPW and SBW were dried under sunlight and ground with a Willey mill, then the SPW and SBW were sieved to be 40-60 mesh in size. The sample was stored in plastic before use. The chemicals were obtained from PT Merck Chemicals and Life Sciences (MCLS) including ethanol and benzene for extracting soluble ethanol-benzene, NaClO₂, and CH₃COOH for holocellulose testing, NaOH and Na₂SO₄ for cellulose testing, H₂SO₄ for lignin testing, NaOH for α -cellulose testing, HCl, H₂SO₄, NaOH, Na₂S₂O₃ for starch testing.

Procedures

Chemical component analysis included ethanol-benzene extractive testing, hot water-soluble extractive testing, holocellulose (cellulose and α -cellulose), lignin, and starch with the standard procedures described in TAPPI T 257 cm-85, TAPPI T 264 om-88, TAPPI T 207 om-93, ASTM 1104-56 1978, Cross and Bevan methods, TAPPI T 222 om-88, and SNI 01-3727-1995, respectively. The proximate analysis for the volatile matter, ash content, and carbon bound was carried out according to SNI 06-3730-199, while the ultimate analysis of C, H, O, N and S contents according to the standard procedures described in ASTM D 5373-14 and ASTM D 4239-14. The degree of crystallinity was analyzed using X-ray diffraction (XRD) spectrometer (SHIMADZU 7000), the functional groups were analyzed using a Fourier transform infrared (FTIR) spectrophotometer (Tensor 37 Bruker), and the surface morphology was analyzed using scanning electron microscope (SEM) (EVO 50 Carl Zeiss). The water (hot water)-soluble compounds of the SPW and SBW were

determined using a gas chromatography-mass spectrometry (GCMS) spectrometer (GCMS-QP2010 PY-2020iS SHIMADZU). The hot water-soluble compounds solution of SBPW and SBW was first dried at 60 °C to obtained extractive solid in which was then analyzed using GCMS. Generally, the SPW and SBW samples were analyzed in triplicate and the average results were reported.

RESULTS AND DISCUSSION

Chemical contents of SPW dan SBW

The results of alcohol-benzene soluble extractives, hot water-soluble extractives, lignin, holocellulose, cellulose, α -cellulose, hemicellulose, and SPW and SBW starch levels are shown in Table 1.

Extractive substances

Extractive substances consist of various organic compounds such as triglycerides, fatty acids and sterols (Nascimento et al., 2013) and phenolic compounds such as tannins (Fava et al., 2006), flavonoids (Sirmah et al. 2009) with low molecular weight which are found in the lumen and part of the cell wall. The amount and type of plant extractive substances depend on their location (Grabner et al. 2005), type of plant, place of growth and climatic conditions (Park et al. 2017). Extractive substances that can dissolve in organic solvents such as benzene alcohol solutions include waxes, fats, resins, oils, and tannins as well as certain components that are not soluble in ether (Sjostrom 1998). Meanwhile, the extraction with hot water can dissolve tannins, gums sugar, coloring agents, and starches (Fengel et al. 1995).

The alcohol-benzene soluble extractive of SPW was 0.77% which is smaller than the SBW extractive of 2.92%. However, the hot water-soluble extractive of SPW was 57.66% which is higher than the SBW hot water-soluble extractive of 4.81% (Table 1). This is because SPW is dominated by parenchyma cells that function as photosynthesis storage for food reserves. In addition, the open SPW pore (Figure 3) facilitates the release of hot water-soluble attractive substances.

Table 1. Chemical contents of SPW and SBW

Chemical content	This study		Utami (2018)	Linggang <i>et al</i> (2012)
	Sago pith waste (%)	Sago bark waste (%)	Sago pith residue (%)	Sago pith residue (%)
Ethanol-benzene extraction	0.8	3.0	-	-
Hot-water extraction	57.7	4.9	-	-
Lignin	6.1	29.4	12	3.9
Holocellulose	45.7	66.8	-	-
cellulose	12.8	44.0	11	23
α -cellulose	12.5	41.9	-	-
Hemicellulose	33.0	22.8	7.6	9.2
Starch	28.9	22.3	63	58

Note: SPW= Sago pith waste; SBW= Sago bark waste

Lignin

Lignin is the main chemical component that forms cell walls together with cellulose and it is dominated by an aromatic group in the form of phenylpropane. Lignin in cells can be found mainly in the middle lamella and primary cell walls. The mechanical properties of cells are influenced by the amount of lignin because lignin causes cell wall rigidity (Sjöström 1998). The SBW lignin test result was 29.38% which is higher than the SPW lignin of 6.11%. This is because SBW is mostly peripheral cells consisting of hard sclereid cells with thick secondary cell walls. Compared with the results of Utami's study (2018), the SPW lignin level in this study was smaller, but the SPW lignin level in the study was higher than the SPW lignin level in Linggang et al. (2012). Meanwhile, the SBW lignin level was smaller than the level of the LW lignin oil palm bark lignin that is equal to 33.61% (Wistara et al. 2017). Lignin is the main component of carbon contributors in activated carbon products with a carbon percentage of about 61%; while the carbon percentages of cellulose and hemicellulose are 42% and 40%, respectively (Cao et al., 2013). The more lignin content, the more aromatic groups are formed (Olcese et al. 2013) and the greater the yield of charcoal (Cao et al. 2013).

Holocellulose

Holocellulose is one of the main components of cell walls and is a total fraction of polysaccharides consisting of cellulose and hemicellulose. Holocellulose content of SPW was 45.74% consisting of 12.75% cellulose, 12.48% α -cellulose, and 32.99% hemicellulose. Meanwhile, the holocellulose content of SBW was 66.74% consisting of 44.00% cellulose, 41.87% α -cellulose, and 22.74% hemicellulose. The SPW holocellulose content is smaller than the SBW, and this is because most SPW consists of non-structural compounds that dissolve in hot water (Table 1). This study is in accordance with the previous work by Wistara et al. (2017) who reported that the SBW holocellulose content is higher than the SPW holocellulose content found in oil palm bark.

Cellulose is a homogeneous compound and its level of purity is often expressed through the percentage of α -cellulose. Cellulose has a strong tendency to generate hydrogen bonds in a straight chain so that cellulose has a crystalline structure, in contrast to amorphous hemicellulose because of its branched structure and more free OH groups (Shmulsky et al., 2011). The number of OH groups can affect the nature of hygroscopy (Brito et al. 2008). SPW cellulose level in this study was greater than the SPW cellulose levels from Utami's study (2018) and smaller than the SPW cellulose level from Linggang et al. (2012). Meanwhile, SPW hemicellulose level was higher than the SPW hemicellulose level from the results of Utami (2018) and Linggang et al. (2012) (Table 1).

Starch

Starch is a carbohydrate and is a food reserve for sago trees which is stored in the pith (Sunartia et al. 2012).

Starch levels increase with age of the sago tree, but after the flowering period, the starch content will decrease because the sago tree will use the starch. Variations in sago tree height result in different starches (Pei-Lang et al. 2006). The main components of starch are about 27% amylose and 73% amylopectin (Karim et al. 2008). The properties of the two types of starch are very different, amylose is a straight-chain polymer with α -1,4-glycosidic bonds while amylopectin is a branched-chain polymer with α -1,4-glycosidic and α -1,6-glycosidic bonds. Amylopectin can react with hot water to generate a gel since it has a branching structure.

SPW starch content (28.85%) is greater than SBW starch content (22.26%). It is due to the granular starch trapped in the lignocellulose matrix (Mohd et al. 2001) or present in the parenchyma cell cavity so that some starch does not dissolve in water during the extraction process of sago flour. The starch content found in this study was smaller than the results of Utami's research (2018) which was 63%, Linggang (2012) which was 58% and Awg-Adeni (2013) which was 30-45%.

Proximate and ultimate analysis of SPW and SBW

Table 2 shows the test results of water content, volatile matter, ash content, fixed carbon, silica, carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) of SPW and SBW.

Determination of water content can be used as an indicator to find out the hygroscopic properties of a material. The SPW water content of 7.15% is higher than the SBW water content of 4.83%. It is because the SPW hemicellulose content is higher than the SBW hemicellulose content. Hemicellulose has more of branched chains and hydroxyl groups than cellulose so that it can bind more water. Therefore, the higher hemicellulose content, the higher its water content. The SPW water content in this study was the same as that of Awg-Adeni (2013), which is 5-7%.

The amount of sago waste biomass volatile matter obtained in this study for SPW and SBW was 84.56% and 81.48% respectively. This amount is substantial when compared to the levels of the volatile matter of charcoal (Novak et al. 2009). It is because biomass is formed by chemical components, which are extractive, holocellulose, and lignin. Hemicellulose decomposition temperature is 210-320°C, cellulose 310-390°C, and lignin 200-550°C (Wu et al. 2009), in which this decomposition temperature is low compared to the test temperature of the volatile matter of 950°C. Heating at a temperature of 950°C will quickly break the chemical compounds of biomass into gases such as CO, CO₂, H₂, and H₂O. Besides, the high level of a volatile matter was also influenced by the oxygen content of biomass, which is easier to reduce compared to the carbon. The amount of oxygen is higher compared to the other elements such as C, H, N, and S (Table 2).

Table 2. Proximate and ultimate analysis of SPW and SBW

Material	Proximate analysis (%)				Silica (%)	Ultimate analysis (%)				
	Moisture	Volatile matter	Ash	Fixed Carbon		C	H	O	N	S
SPW	7.2	84.6	3.0	12.8	2.0	37.9	6.5	51.10	0.13	0.11
SBW	4.9	81.4	1.3	18.7	1.3	44.6	6.37	47.75	0.03	0.12

SPW= Sago pith waste; SBW= Sago bark waste

Determination of ash content aimed to discover the content of metal oxides in sago waste biomass after being heated at high temperatures. The ash content of sago waste biomass obtained in this study was 3.04% and 1.30% for SPW and SBW respectively, lower than the research results by Kumoro et al. (2008) which was 4.16%. The number of minerals that do not decompose at high-temperature influences ash content in biomass. Ash can be divided into two fractions, soluble fraction and insoluble fraction. Insoluble inorganic fractions are generally silica. Ash content of SPW is higher than SBW; this is because parenchyma cells dominate SPW. According to Sjoström (1995), ash contains many metals such as Calcium and Potassium in the form of oxalate crystals stored in axial parenchyma.

The silica content of sago waste biomass obtained in this study was 2.03% and 1.25% for SPW and SBW respectively, with silica/ash content ratio of 67% and 96% for SPW and SBW respectively. The ratio indicates that most of the minerals in sago waste biomass are silica, especially in SBW. The ratio of silica/ash content of SBW is higher than SPW and also higher than the research results on *Gramineae*, such as bagasse 92% (Sapawe et al. 2018). In *Gramineae* plants, silica plays a role in straightening the leaves (Tripathi et al. 2017) while in other plants, silica plays a role in increasing plant growth (Artyszak 2018). Silica in biomass can reduce the calorific value (Demirbas 2007) and dulls saw (Sommer et al. 2015).

The ultimate analysis results showed that the amount of carbon (C) in SPW was lower than SBW, while the amount of oxygen (O) in SPW was higher than SBW. The amount of lignin and hemicellulose influence the amount of carbon (C) and oxygen (O) (Yang et al. 2007). Lignin contains more carbon (C) so the higher the lignin, the greater the carbon (C). Hemicellulose with branching structure and its ability to absorb H₂O molecules can affect the amount of oxygen (O), so the more hemicellulose and water content, the higher the oxygen (O). The content of hydrogen (H), nitrogen (N), and sulfur (S) of SPW and SBW were relatively similar and very low. Hydrogen (H) was only about 6%, while nitrogen (N) and sulfur (S) were lower than 1%. The high carbon content (C) of biomass can increase the yield of charcoal in the carbonization process, but the high carbon (C) and low nitrogen (N) will affect biomass decomposition, the higher the C/N ratio, the more difficult the decomposition (Zhou 2016). This decomposition process can hamper the use of biomass as compost because of the long composting time. The ultimate test results of this study are in line with the study of Danish

et al. (2015), which are low content of N and S, lower than 1% and dominated by carbon (C) and oxygen (O).

XRD analysis (X-ray diffraction) of SPW and SBW

XRD analysis has long been used to determine the structure of biomass (Ahvenainen et al. 2016) such as crystalline regions, amorphous regions, and crystal forms. The results of XRD analysis of SPW and SBW showed that the degree of crystallinity of SPW was 15.04%, lower than the degree of crystallinity of SBW 47.28% (Table 3). The size of the crystalline area depends on the nature of the raw material such as the amount of cellulose (Kontturi et al. 2011). Cellulose is a straight-chain polysaccharide that has three hydroxyl groups per glycoside molecule that tend to form glucose bonds, either Intra or intermolecular glucose. Hydrogen bonds at C2, C3 and C6 atoms (Fan et al. 2012) affect water absorption (Awa et al. 2014) and crystallinity (Brito et al. 2008) where the more cellulose, the higher the crystallinity. (Rezende et al. 2011). Besides cellulose, water content also affects the crystallinity of biomass (Sugino et al. 2007). The more water content, the lower the degree of crystallinity (Poletto et al. 2013).

The crystal structure of sago waste is monoclinic, characterized by the main peak of the 2 theta diffraction angle around 15-17° and 21-22° (Wada et al. 2010). Figure 1 shows the high intensity of SBW at a diffraction angle of 2 theta 22°; this was due to SBW cellulose content which is higher than SPW cellulose content. The degree of crystallinity of biomass affects the nature of hydrolysis. The higher the degree of crystallinity, the more difficult process of hydrolysis occurred and vice versa (Park et al. 2010). The lower degree of crystallinity of SPW causes it to easily hydrolyzed so that it is easier in the process of saccharification (Agrawa et al. 2014).

FTIR (Fourier Transform Infrared Spectrophotometer) Analysis of SPW and SBW

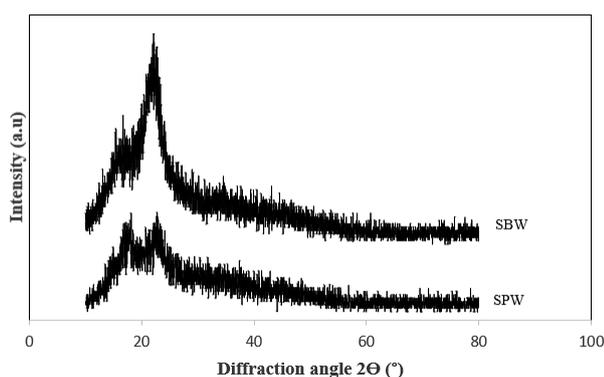
FTIR analysis is used to observe the functional groups of organic and inorganic elements qualitatively. A functional group is a group of one or more distinctive and charged atoms, which responsible for the characteristics of a chemical reaction. Functional groups are determined based on vibrations that occur at specific wavenumbers.

Table 3. XRD Analysis of SPW and SBW

Material	Crystallinity degree (%)
SPW	15.04
SBW	47.28

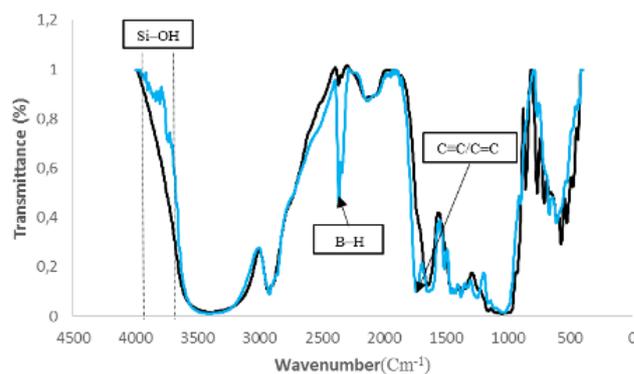
Table 4. FTIR Analysis of SPW and SBW

Material	Wavenumber (cm ⁻¹)
SPW	3399.49-2929.13-2362.84-2151.27-1645.55-1427.11-1051.82-859.84-766.32-709.74-574.22-528.01-477.74-437.45
SBW	3900.27-3837.06-3821.03-3801.29-3730.94-3398.97-2920.88-2361.36-2337.79-2132.23-1866.99-1736.75-1648.31-1512.14-1427.00-1379.69-1249.37-1035.67 898.15-768.60-668.45-611.61

**Figure 1.** XRD images of SPW and SBW

The absorption intensity of these two types of biomass is different (Figure 2). The intensity of the SPW absorption was more in the 1,000-500 cm⁻¹ band while the SBW absorption intensity was more in the 2,000-1,000 cm⁻¹ and 4,000-3,000 cm⁻¹ bands. The SBW absorption intensity was high at wavenumber 1,736.75 cm⁻¹, which is indicated as a functional group of aldehydes C≡C and ester C=C. This was because SBW's lignin was higher than SPW (Table 1). Cellulose and hemicellulose were indicated by absorption at wavenumber of 1,400-875 cm⁻¹, lignin at 1,700-1,200 cm⁻¹ and extractive at 1,700 cm⁻¹ (Park et al. 2017). Cellulose is indicated by the high absorption of the-OH and C-O bonds, hemicellulose is indicated by the absorption of compounds with C=O double bonds (Yang et al. 2007) while lignin is indicated by the high absorption of single bonds and carbon double bonds. SBW absorption intensity was also higher than SPW at a wavenumber of 2,350-2,650 cm⁻¹ which is indicated as a functional group of boron B-H stretching compounds. Also, the intensity of SBW vibrations at 4,000-3,000 cm⁻¹ wavenumber is indicated as a functional group of silicate Si-OH stretching compounds. This was due to the high silica/ash ratio of SBW which is 96%.

Some minerals were also identified as phosphorus and sulfur compounds (Table 4). Vibration at wavenumber 1,050-870 cm⁻¹ was indicated as a functional group of the aromatic phosphorus compound P-O stretching in sago bark, and vibrations at wavenumber 1,060-1,020 cm⁻¹ were indicated as a functional group of sulfur S=O stretching compounds in sago waste and sago bark (Stuart 2004). Sulfur, nitrogen, and phosphorus are the elements needed for plant growth (Mahajan et al. 2004). Thus sago waste has the potential to be used as organic fertilizer.

**Figure 2.** FTIR analysis images of SPW (---) and SBW (—)

SEM (scanning electron microscope) Analysis of SPW dan SBW

Morphological observations can be done by using scanning electron microscope analysis (Müller 2010). The results of the SEM micrograph analysis showed that the surfaces of the two biomasses were different (Figure 3). The surface morphology of the SBW is not porous; this was because the SBW pores were covered with materials that are indicated as mineral, while the SPW surface had small pores and thin cell walls. The difference in surface porosity of the SPW and SBW caused the extractive levels of hot water solubility of SBW to be less (Table 2). SBW starch was largely insoluble during hot water extraction, while SPW was entirely soluble in hot water extraction. Pores are a means of extracting extractive substances and means for the entry of desired substances such as chemicals in saccharification and composting so that these chemicals can react with cell walls.

GCMS results of hot water-soluble extractive SPW and SBW

The results of SPW and SBW hot water-soluble extracts were not only quantitatively different (Table 1), but also qualitatively different (Figure 1). The SPW hot water-soluble extract had sediment and was slightly colored, while the SBW hot water-soluble extract had no sediment and was colored. To determine the constituent compounds of SPW and SBW soluble extracts, a Py-GC/MS analysis was performed at 400 °C (Table 5 and Table 6).

The GCMS results of the SPW hot water-soluble extractive showed the presence of several dominant compounds (Table 5) such as Hydrazine, 1,1-dimethyl- (CAS) N, N-Dimethylhydrazine; 1,3-Dioxane, 6-Hydroxy-

2,4-Dimethyl; cis-1,3-Dideuterio-1,3-cyclohexandiamine; and L-Serine (CAS) Serine, L. While the dominant compounds in SBW hot water-soluble extractive (Table 6) were 1,6-Anhydro-Beta-D-Glucopyranose (Levoglucosan); 2-Furancarboxaldehyde, 5-(hydroxymethyl)-(CAS) HMF; and 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-(CAS) 3,5-Dihydroxy. GCMS results of SPW hot water-soluble extractive showed no sago waste lignin component

derivatives, whereas the SBW hot water-soluble extractive showed a derivative of lignin components such as Phenol, 2-methoxy-(CAS) Guaiacol and Benzaldehyde, 4-hydroxy-3-methoxy-(CAS) Vanillin (Kuroda et al. 2001). This was because SBW contains more lignin contents compared to SPW. SPW hot water-soluble extractive derivatives contain more nitrogen, alcohol and sugar groups, while SBW contains more phenol compounds.

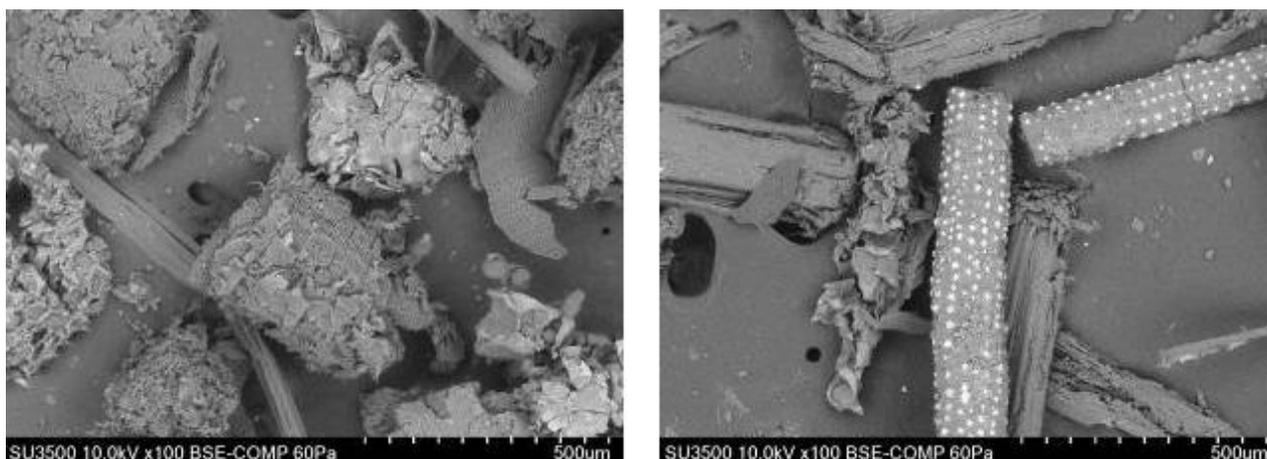


Figure 3. Scanning electron microscopy surface images of sago waste: A. SPW (Sago pith waste), B. SBW (sago bark waste)

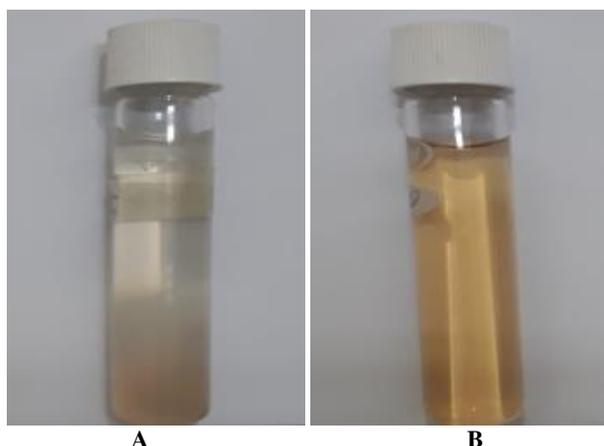


Figure 4. Hot-water extraction of sago waste: A. SPW (Sago pith waste), B. SBW (sago bark waste)

Hydrazine in SPW hot water-soluble extractive is organic hydrazine because it comes from biomass. Hydrazine can be synthesized from ammonia and hydrogen peroxide in the peroxide process (sometimes it is called the Pechiney-Ugine-Kuhlmann process, the Atofina-PCUK

cycle, or the ketazine process) (Schirrmann 2002). These compounds are categorized as inorganic compounds with the chemical formula N_2H_4 , called diamidogen. This is a simple pnictogen hydride, and is a colorless, flammable liquid with a smell like ammonia and is poisonous (PubChem). Hydrazine compounds can be effective as active ingredients in blends with other agricultural chemicals such as insecticides, mythitis, nematicides, fungicides, antiviral agents, attractants, herbicides or plant growth regulators (Toki et al. 1994).

For conclusion, the characterization of the SPW and SBW was successfully carried out in which the results show that both SPW and SBW could potentially be used as: (i) carbon source for the solid-state fermentation for organic acids (i.e. acetic acid), biofuel (i.e. bioethanol) and protein (i.e. enzyme such as laccase and cellulase) productions and (ii) the production of biochars and activated carbons. In addition, the SPW also contained very large hot-water soluble compounds dominated by hydrazine compounds which are potential for production of organic hydrazine. Thus, the SPW and SBW could be utilized for the economic benefits as well as solving environmental problems. The utilization of these wastes will be the subject of future studies.

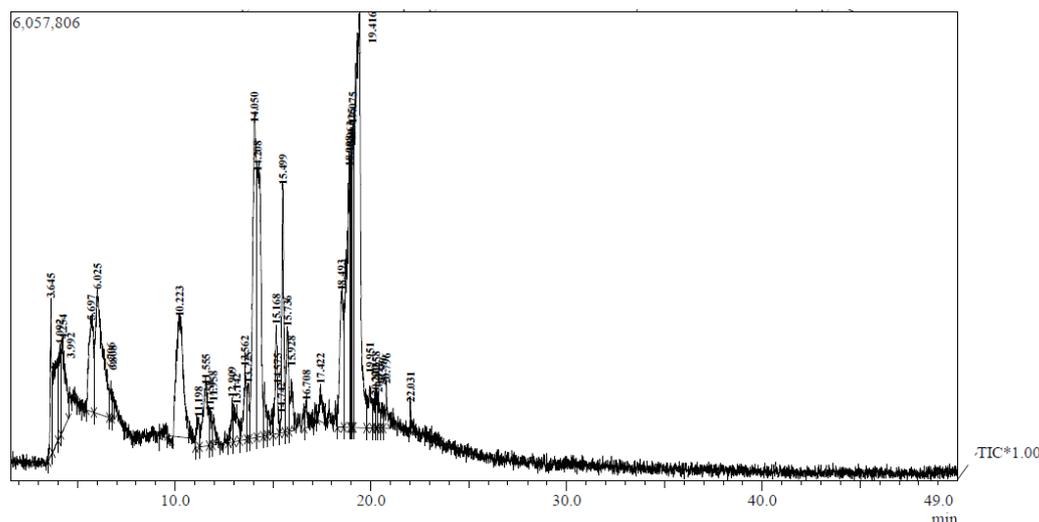


Figure 5. The chromatogram of 400 °C pyrolyzate from SPW hot water-soluble extracts by Py-GC/MS

Table 5. Chemical components of 400 °C pyrolyzate from SPW hot water-soluble extracts by Py-GC/MS

Peak number	Retention time (minute)	Area (%)	Compound
1	3.645	1.74	2-Propynoic
2	3.992	2.8	Oxirane, 2,3-diphenyl-(CAS) 1,2-Epoxy-1,2-Diphenylethane
3	4.092	1.55	3-Hydroxy-Pentanedioic Acid
4	4.254	2.7	Oxirane (CAS) Epoxyethane
5	5.697	3.09	Acetic acid (CAS) Ethylic acid
6	6.025	6.83	Acetic acid, anhydride (CAS) Acetic oxide
7	6.706	0.37	1-Propanol, 2-methyl-(CAS) Isobutyl alcohol
8	6.808	0.38	1,1-Heptanediol, diacetate (CAS)
9	10.223	6.16	2-Furanmethanol (CAS) Furfuryl alcohol
10	11.198	0.57	1-Propanamine, N,2-dimethyl-N-nitroso-(CAS) Methyl Isobutyl Nitrosamine
11	11.555	2.27	Cyclopentanone, 2-methyl-(CAS) 2-Methylcyclopentanone
12	11.758	0.63	Pentane,1-chloro-(CAS) 1-Chloropentane
13	11.958	0.41	Iso Butyl Alcohol
14	12.909	0.6	Lactic acid, monoanhydride with 1-butane boronic acid, cyclic ester (CAS) Lactic Acid N-Butyl
15	13.142	0.9	4-Pyrimidinol, 5-(aminomethyl)-2-methyl-,
16	13.562	1.56	3-Nitro-2-pentanol
17	13.725	0.8	Butane, 2-methyl-(CAS) Isopentane
18	14.05	8.73	1,3-Dioxane, 6-Hydroxy-2,4-Dimethyl-
19	14.208	8.2	cis-1,3-Dideuterio-1,3-cyclohexandiamine
20	14.575	0.73	1,7-Nonadien-4-Ol, 4,8-Dimethyl-
21	14.742	0.42	N-(2-Methyl-2h-Tetrazol-5-Yl)-Acetamide
22	15.168	1.77	6-Dimethylamino-3,5-Dihydroxy-1,2,4-Triazine
23	15.499	3.68	2-Butene-1,4-diol, (Z)-(CAS) cis-Butenediol
24	15.736	1.89	2-Furancarboxaldehyde, 5-(hydroxymethyl)-(CAS) HMF
25	15.928	1.01	6-Dimethylamino-3,5-Dihydroxy-1,2,4-Triazine
26	16.708	0.49	2-Propenoic acid, 2-(acetlamino)-(CAS) .Alpha.-Acetaminoacrylic Acid
27	17.422	0.84	2-D-2-Pentadecyl-1,3-Dioxolane
28	18.493	3.63	Acetic acid, pentyl ester (CAS) n-Amyl acetate
29	18.908	7.44	L-Serine (CAS) Serine, L
30	18.963	1.71	1-(P-Toluidino)-1-Deoxy-B-D-Idopyranose
31	19.025	1.74	Formic acid, propyl ester (CAS) n-Propyl formate
32	19.075	2.39	Ethanamine, N-methyl-N-nitroso-(CAS) N-Nitrosomethylethylamine
33	19.416	18.24	Hydrazine, 1,1-dimethyl-(CAS) N,N-Dimethylhydrazine
34	19.951	1.1	Ethane, 1,1,1-triethoxy-(CAS) Triethyl orthoacetate
35	20.22	0.56	1-(1-Propenylthio)Propane
36	20.258	0.35	Serine Thiohydantoin
37	20.392	0.44	4-Nonynoic acid, methyl ester (CAS) Methyl 4-Nonynoate
38	20.596	0.33	1,6-Hexanediol (CAS) Hexamethylene glycol
39	20.796	0.8	Nonanoic acid (CAS) Nonoic acid
40	22.031	0.16	2-Cyclopentene-1-undecanoic acid (CAS) 11-(Cyclopent-2-En-1-Yl)

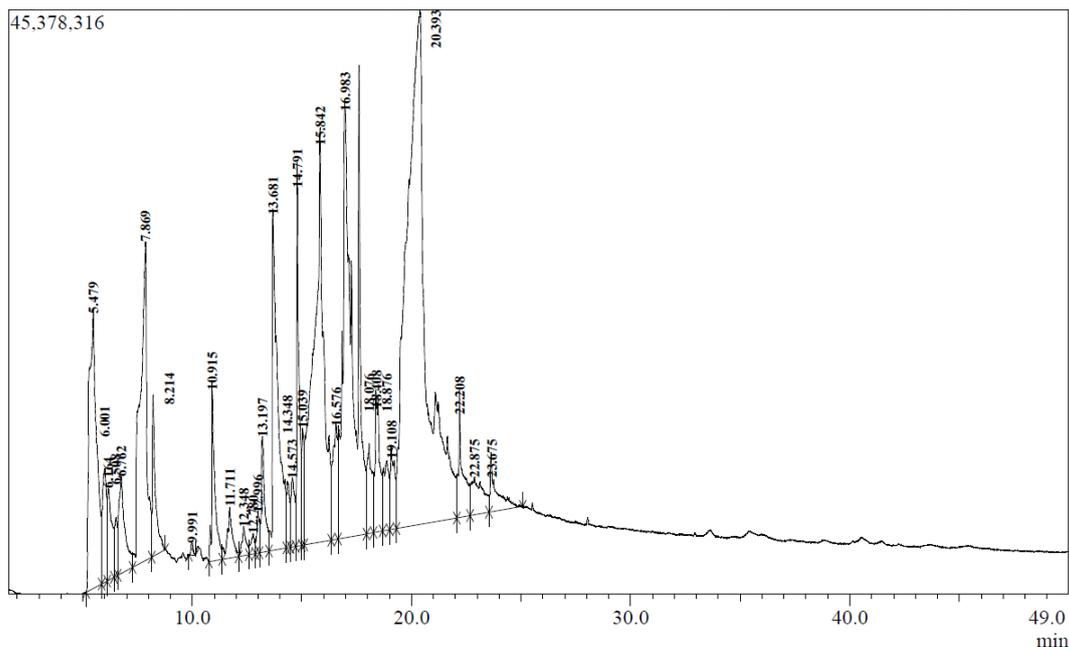


Figure 6. The chromatogram of 400 °C pyrolyzate from SBW hot water-soluble extracts by Py-GC/MS.

Table 6. Chemical components of 400 °C pyrolyzate from SBW hot water-soluble extracts by Py-GC/MS

Peak number	Retention time (minute)	Area (%)	Compound
1	5.479	6.13	Formamide (CAS) Methanamide
2	6.001	1.36	2-Octanamine, N-(1-methyl heptyl)-(CAS) Bis-(1-Methyl)Heptylamine
3	6.164	1.22	Acetic acid, methyl ester (CAS) Methyl acetate
4	6.508	0.50	1-Propanamine, 2-methyl-(CAS) iso-Butylamine
5	6.762	1.74	Furan, 2-methyl-(CAS) 2-Methylfuran
6	7.869	6.25	Acetic acid (CAS) Ethylic acid
7	8.214	1.42	2-Propanone, 1-hydroxy-(CAS) Acetol
8	9.991	0.08	Butane, 2-propoxy-(CAS) Ether, 2-Butyl Propyl
9	10.915	1.64	2-Furancarboxaldehyde (CAS) Furfural
10	11.711	0.75	Butane, 2,2-dichloro-3-methyl-(CAS) 2,2-Dichloro-3-methyl butane
11	12.348	0.35	2-Acetyl Furan
12	12.780	0.23	2-D-2-Pentadecyl-1,3-Dioxolane
13	12.996	0.28	Hexane, 2,5-dimethyl-(CAS) 2,5-Dimethylhexane
14	13.197	1.24	5-methyl furfural
15	13.681	5.58	Benzenesulfonic acid, 4-hydroxy-(CAS) Benzenesulfonic acid,
16	14.348	0.59	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-(CAS) Corylon
17	14.573	0.74	Sulfurous acid, dibutyl ester (CAS) Di-N-Butyl Sulphite
18	14.791	2.56	Phenol, 2-methoxy-(CAS) Guaiacol
19	15.039	0.70	Phenol, 4-methyl-(CAS) p-Cresol
20	15.842	12.16	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-(CAS) 3,5-Dihydroxy
21	16.576	1.61	5-Formyl-2-furfurylmethanoate
22	16.983	13.68	2-Furancarboxaldehyde, 5-(hydroxymethyl)-(CAS) HMF
23	18.076	1.30	3-Octen-1-ol, acetate, (Z)-(CAS)
24	18.408	2.02	Benzaldehyde, 4-hydroxy-3-methoxy-(CAS) Vanillin
25	18.876	1.13	1-(4-Chlorophenylsulfonyl)-2,3-dihydro-5-methoxy-3-oxoindole
26	19.108	1.07	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-(CAS) Acetovanillone
27	20.393	29.77	1,6-Anhydro-Beta-D-Glucopyranose (Levogluconan)
28	22.208	1.56	Hexadecanoic acid (CAS) Palmitic acid
29	22.875	1.28	Octadecanoic acid, 2-propenyl ester (CAS) Allyl Octadecanoate
30	23.675	1.08	Heptadecene-(8)-Carbonic Acid-(1)

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