

## **CHEMICAL COMPOSITION AND POTENTIAL USES OF *LEUCAENA LEUCOCEPHALA* STEM BARK**

RAFIDAH MD SALIM, JAHIMIN ASIK, MOHD SANI SARJADI, LIEW KANG CHIANG  
UNIVERSITY OF MALAYSIA SABAH  
MALAYSIA

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### **ABSTRACT**

*Leucaena leucocephala* stem bark that was eleven years old was studied for its chemical composition and usage. The samples were subjected to chemical analyses based on ASTM standard procedures after being air-dried for several days. The results found that the bark of *L. leucocephala* has a pH value of 6.04 and that the solubility of the bark in 1% NaOH alkali is the highest compared to the solubility in hot water (14.45%) and cold water (14.36%), while the chemical composition of the bark of *L. leucocephala* was ash (15.76%); extractives (8.39%); holocellulose (132.85%); hemicellulose (103.66%); cellulose (29.19%) and lignin (38.24%). Based on the findings, *L. leucocephala* bark was less acidic. When used as a source of carbohydrates, bark has a high solubility, and its chemical composition may have an impact on how quickly it burns when it is pyrolysed.

**KEYWORDS:** Acidity, solubility, chemical composition, bark.

### **INTRODUCTION**

In terms of chemical composition, bark is different from wood. In general, bark is composed of polysaccharides (cellulose, hemicelluloses), pectic materials, phenolic polymers such as lignin and high molecular weight tannins, and cross-linked polyesters such as suberin and cutin. In general, the holocellulose in bark has a larger percentage of mannose, and some conifer barks include lignin that is more strongly crosslinked than wood lignin (Feng et al. 2013). Bark can also contain some low molecular weight components, such as fatty acids, resins, and low molecular weight phenolics. The amounts of extractives and ash in bark were significantly higher than those in wood. Most of the extractives in bark are comparable to those in wood, with the main distinction being that many barks contain more polyphenols and suberin with a high molecular weight (Chow et al. 2008). Bark has a higher concentration of aromatic

components, such as tannin and lignin, as well as lipophilic extractives (Kim et al. 2005). On the other hand, the aromatic polyol structural elements in bark encourage its use in the manufacturing of phenol formaldehyde (PF) resins and foam.

Bark is used far less frequently than other major wood waste categories, such as slab and sawdust. Numerous new uses for wood bark have been studied, including as absorbents for pollutants (Dalahmeh et al. 2012), a filler for phenolic resins when used in plywood (Eberhardt and Reed 2006), a formaldehyde or metal ion absorber (Takano et al. 2008), and a proanthocyanidin with antioxidant action (Ku and Mun 2007), among others. The use of bark in the manufacture of chemicals and materials, such as wooden panels, tannins, resins and foams, bio-oils, etc., as well as for medicine, colours, spices, incense, cork, animal bedding, and the absorption of pollutants, is widespread. The review focuses on the use of bark in the production of chemicals and materials, specifically tannins, resins, and foams, as well as the thermochemical conversion of bark (through phenolysis, direct liquefaction, and pyrolysis) and the usage of the end products of bark thermochemical conversion (Feng et al. 2013).

Compared to wood, the chemical characterization of bark has received little attention, despite being crucial for assessing prospective uses. Bark varies from wood in that it contains more extractives, such as polyphenols and organic solvents, and is water soluble, as well as more ash, an inorganic substance (Pereira et al. 2003). For an accurate assessment of acidity, which is influenced by external conditions, the pH value of bark is needed. The acidity of bark is one of the most significant ways of expressing the pH value (Steindor et al. 2011).

*Leucaena leucocephala* spp., often known as Petai belalang, is a rapidly growing species of leguminous shrub that has the potential to be used commercially as a plantation species to produce pulp in the pulp paper industry. This species is frequently used to produce gum, furniture, construction lumber, poles, etc. This species is grown in Malaysia as a cover crop and green manure and for land management, reforestation, erosion control, and conservation of water. *L. leucocephala* bark has a density of approximately  $690 \text{ kg m}^{-3}$  (medium to hardwood class lumber), presenting Malaysian hardwood species (Ahmad et al. 2011).

Local *Leucaena leucocephala* bark from the bottom stem to the starter first tree branch portion was employed as the study's source material. When peeling the bark off the trunk in a sawmill or other wood-based industry, this part typically produces a significant amount of waste or residue. Before performing the experiment, the bark was thoroughly mixed. The objectives of this study were to identify the characteristics of the pH value of bark, assess the potential of *L. leucocephala* stem bark as a carbohydrate resource, and examine the potential use of a significant component of *L. leucocephala* stem bark for chemical utilization.

## MATERIAL AND METHODS

### Preparation of samples

*Leucaena leucocephala* bark that was eleven years old was employed in this investigation. The tree was cut down at UMS in Kota Kinabalu, Sabah, Malaysia. Within the UMS campus, this tree's location was surrounded by a wooded area where the air is clean. Only the bark from

the stem of the tree was obtained after the tree's trunk had been carefully peeled, and it was identified by botanist experts from the Forestry Division, UMS. The Wood Chemistry Laboratory received all the samples for further processing.

The bark was carefully cleaned to eliminate dirt, and then it was allowed to air dry in a lab environment for two to three weeks away from direct sunshine or heat ( $24 \pm 2^\circ\text{C}$ ). Using a laboratory grinder, the dried stem was flaked, chipped, and ground into a coarse powder. Powder that was kept on a  $250\ \mu\text{m}$  mesh sieve after passing through a  $500\ \mu\text{m}$  mesh sieve was utilized for chemical analysis. The outer and inner bark were not distinguished in this investigation. This is mostly because divorce is expensive and complicated. Additionally, maintaining these fractions is crucial to boosting the skin's phenolic content and enhancing the characteristics of resins (Xavier et al. 2012).

### **Chemical analyses of bark**

Prior to chemical analysis, the bark powder was air dried for several days to obtain a constant weight. According to the ASTM (American Society Testing and Material standard) procedure, the pH (E70 2019), solubility in hot and cold water (D1110-84 2001), 1% NaOH (D1109 2001), ethanol-toluene solubility (D1105 2001), ash (D110-84 2001), holocellulose (D1104 1985), cellulose (D1103 1978) and lignin (D1106 2001) content of *Leucaena leucocephala* bark were all determined.

#### *Determination of pH*

Using an analytical balance, 2 grams of bark powder were precisely measured. In a tall beaker with a 50 ml capacity, distilled water (20 ml) was added, and the solution was thoroughly mixed before being left to stand for two hours. After calibrating the pH meter, the pH of the bark was then determined using an electrode submerged in the solution. When the pH is 7, the substance is considered neutral; when the pH is less than 7 or greater, the substance is deemed acidic or alkaline, respectively.

#### *Hot water solubility*

In an Erlenmeyer flask containing 2 g of bark powder, 100 ml of distilled water was added (moisture content determined). The flask was slowly heated in a boiling water bath for three hours with the water outside the flask just above the level of the water inside. The material was extracted via suction, put through a crucible, and then given a hot water wash. Before being cooled in desiccators and weighed, the residue was dried in an oven at  $103 \pm 2^\circ\text{C}$ . Eq. 1 was used to compute the hot water solubility (HW) percentage of bark.

$$\text{HW (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

where:  $w_1$  is the weight of the moisture-free bark powder (g) and  $w_2$  is the weight of the oven-dried residue following hot water extraction (g).

#### *Cold water solubility*

Approximately 400 ml of digest was mixed with 2 g of bark powder (known moisture content) in a 400 ml beaker at a temperature of  $23 \pm 2^\circ\text{C}$  for 48 h while stirring frequently.

The material was filtered into a weighted, medium- or coarse-porosity glass crucible, cleaned with cold distilled water, and then heated to  $103 \pm 2^\circ\text{C}$  for 4 h. The crucible residue was measured after cooling in desiccators. Eq. 2 was used to determine the bark's percentage of cold-water solubility (CW).

$$\text{CW (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (2)$$

where:  $w_1$  is the weight of the moisture-free bark powder (g) and  $w_2$  is the weight of the oven-dried residue following cold-water extraction (g).

#### *1% NaOH solubility*

Approximately 2 g of bark powder and 100 ml of a 1% NaOH solution were thoroughly mixed (200 ml tall beaker). The beaker was then placed in a boiling water bath for 1 hour while being stirred continuously at 10, 15, and 25 min. The material was sieved using a crucible and suction before being rinsed with 100 ml of hot water and then 50 ml of 10% acetic acid. The crucible and its contents were weighed after being dried at  $103 \pm 2^\circ\text{C}$  until constant weight and chilled in desiccators. Bark's percent solubility in a 1% sodium hydroxide solution (NaOH) was calculated using Eq. 3.

$$\text{NaOH (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (3)$$

where:  $w_1$  is the weight in grams of the moisture-free bark powder (g) and  $w_2$  is the weight of the oven-dried residue that was treated with NaOH solution (g).

#### *Determination of ash content*

A little over 2 g of bark in a crucible was weighed, dried for an hour at  $103 \pm 2^\circ\text{C}$  in an oven, cooled in desiccators, and then weighed. The crucible and its contents were then placed in a muffle furnace to slowly heat up until the final ignition temperature of  $590 \pm 10^\circ\text{C}$  was reached after 30 min. The crucible was removed, cooled, and weighed. Using Eq. 4, the percentage of ash content in the bark was determined.

$$\text{Ash (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (4)$$

where:  $w_1$  is the weight of the ash (g) and  $w_2$  is the weight of the oven-dried bark (g).

#### *Determination of moisture content*

Approximately 2 g of bark sawdust (in a crucible) was dried in an oven at  $103 \pm 2^\circ\text{C}$  for two hours. After cooling in desiccators, the contents were weighed. It continues to dry for an additional hour until the weight remains steady. Eq. 5 is used to compute the percentage of bark moisture content (MC) using an air-dried specimen.

$$\text{MC (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (5)$$

where:  $w_1$  is the weight in grams of the air-dried bark powder,  $w_2$  is the weight in grams of the oven-dried bark powder, and the X factor is equal to  $(100 - MC)/100$ .

#### *Ethanol-toluene solubility*

The Whatman thimble contained approximately 2 g of bark, which was added to the Soxhlet extraction flask. A 150 ml solution of ethanol was used for extraction (427 ml of toluene was converted to 1 l by adding ethanol). The solvent blends smoothly. Six siphonings were performed during the six hours of extraction. The flask was then evaporated and dried for 1 h at  $103 \pm 2^\circ\text{C}$  in an oven before being cooled and weighed. Eq. 6 was used to calculate the proportion of bark that was soluble in ethanol-toluene (ET).

$$\text{ET (\%)} = \frac{w_2}{w_1 P} \times 100 \quad (6)$$

where:  $w_1$  is the weight of the moisture-free bark powder (g),  $w_2$  is the weight of the oven-dried residue (g), and P is the proportion of the air-dried specimen.

#### *Determination of holocellulose content*

Approximately A 250 ml tall beaker was filled with approximately 2 g of air-dried, extractive-free bark powder after being weighed. The flask was added to 100 ml of distilled water, 1.5 g of sodium chlorite, and 5 ml of 10% acetic acid before being heated in a hot water bath at a temperature of  $70^\circ\text{C}$ . Every 5 min, the solution in the flask was stirred with a glass rod to ensure that it was just below the level of the bathwater. The flask was sealed with a rounded, flat glass.

After adding 1.5 g of sodium chlorite for the first 30 min, approximately 5 ml of 10% acetic acid was applied. The last addition of sodium chlorite was added after repeating this step three more times. The suspension was then chilled in an ice bath before being filtered into a weighed crucible with porosity 1. After being cleaned with chilled distilled water, the residue (which is white in color) was eventually cleaned with acetone. After being air dried for a day to remove any acetone, the residue was transported to a desiccator. Eq. 7 was used to calculate the amount of holocellulose in the bark.

$$\text{Holocellulose (\%)} = \frac{Y_3}{W_3 X} \times 100 \quad (7)$$

where:  $Y_3$  = weight of air-dried holocellulose (g),  $= Y_2 - Y_1$  = (weighed crucible & air-dried holocellulose - weighed crucible) (g), and  $W_3 X$  = weight of alcohol - toluene solubility, oven-dried bark (g).

#### *Determination of cellulose content*

The previous experiment's air-dried holocellulose was added to a 250 ml tall beaker along with 15 ml of 17.5% NaOH. For one minute, the solution was stirred with a magnetic stirrer. The solution was agitated for 45 s after 10 ml more of 17.5% NaOH was added. After stirring for 15 s and adding 10 ml of 17.5% NaOH, the liquid was allowed to stand for 3 min. After stirring for 3 min, 10 ml more of the 17.5% NaOH was added. This procedure was carried out

three more times (total time 15 min). After 30 min (a total of 45 min), 100 ml more of distilled water was added and stirred into the solution. The solution was then allowed to stand for 30 min (a total time 75 min).

The mixture was filtered into a glass crucible that was measured (coarse porosity 3). The beaker and residue were then cleaned with 650 ml of distilled water at 20°C after being rinsed with 25 ml of 8.3% NaOH solutions. Filtration was stopped, and 2N acetic acid was added to the crucible for 5 min. The remaining material was filtered once more, and then washed with distilled water. The leftover material was oven-dried at  $103 \pm 2^\circ\text{C}$  for 24 h before being cooled and weighed. Eq. 8 was used to calculate the alpha-cellulose content of bark as a percentage.

$$\text{Cellulose (\%)} = \frac{Z_2}{Z_1} \times 100 \quad (8)$$

where:  $Z_1$  is the sample's oven-dried weight (g), and  $Z_2$  is the sample's oven-dried weight (cellulose) (g)

#### *Determination of lignin content*

After being accurately weighed, 1.4 g of air-dried extractive free bark powder was placed into a 50 ml tall beaker. Carefully add 15 ml of 72% sulfuric acid with a pipette and stir the mixture with a tiny glass rod (which is left in beaker). The beaker was submerged in cold water for two hours at 20°C while being agitated every 10 min. The mixture was put into a 1 L Erlenmeyer flask that held 560 ml of hot distilled water at the conclusion of the experiment. The sample was heated on a hot plate for four hours while being boiled in an Erlenmeyer flask connected to a condenser reflux.

Following refluxing, the insoluble lignin was collected by filtration through the crucible's known weight (porosity 4). The residue was washed with 500 ml of hot water, dried for 24 h at  $103 \pm 2^\circ\text{C}$ , chilled, and weighed. Eq. 9 reported the lignin content as a percentage by weight of the dried sample.

$$\text{Lignin (\%)} = \frac{W_4 - W_3}{100 W_2} \times (100 - W_1) \quad (9)$$

where:  $W_1$  represents the percentage of alcohol-toluene extractive,  $W_2$  the weight of oven-dried extractive free bark powder,  $W_3$  the weight of oven-dried crucible, and  $W_4$  the weight of oven-dried residue and crucible (g).

#### **Statistical analysis**

The data are expressed as the mean and standard deviation, and every test and analysis included at least six replicates. The means of these data were separated using the least significant difference (LSD) test, and statistical significance was attained at  $p < 0.05$  when using SPSS 16.0 to conduct ANOVA.

## RESULTS AND DISCUSSION

### Physical and chemical analysis of *Leucaena leucocephala* stem bark

*Leucaena leucocephala* bark's pH level, solubility in hot, cold, and 1% NaOH, as well as its composition in terms of ash, holocellulose, hemicellulose, alpha-cellulose, and lignin, are all shown in Tab. 1. Based on the variations between holocellulose and alpha cellulose, the amount of hemicellulose was determined.

Tab. 1: Chemical composition and solubility of *L. leucocephala* bark.

pH		<b>6.04</b> ± 0.72
Solubility (%)	Cold water	<b>11.06</b> ± 1.48 <sup>a</sup>
	Hot water	<b>14.45</b> ± 2.29 <sup>b</sup>
	1% NaOH	<b>41.36</b> ± 0.66 <sup>c</sup>
Composition (%)	Ash	<b>15.76</b> ± 0.42 <sup>a</sup>
	Extractive	<b>8.39</b> ± 0.44 <sup>a</sup>
	Holocellulose	<b>132.85</b> ± 21.45 <sup>d</sup>
	Hemicellulose	<b>103.66</b> ± 18.87 <sup>c</sup>
	Cellulose	<b>29.19</b> ± 0.50 <sup>b</sup>
	Lignin	<b>38.24</b> ± 3.02 <sup>b</sup>

Notes: N - stands for the sample size (N = 6), ± values represent standard deviations, and  $p < 0.05$  indicates that means with the same letter are not significantly different.

The analysis of variance (ANOVA) of the stem bark of *L. luecocephala* is displayed in Tab. 1. The solubility of bark varied significantly between cold water, hot water, and 1% NaOH at  $p < 0.01$ . On the other hand, there was no discernible variation in the chemical characteristics of bark between the extractive and ash concentrations. Alpha-cellulose and lignin did not significantly differ from one another at  $p < 0.05$ , while the holocellulose content was significantly different from the hemicellulose, alpha-cellulose, and lignin contents at  $p < 0.01$ .

### Bark acidity

The result indicates that the pH of *L. luecocephala* bark is 6.04, which is regarded as having the least acidity (Tab. 1). The location might have an impact on how acidic the bark of *Luecocephala* is. Bark from *L. luecocephala* may be less acidic since it grows in less polluted, forested sections of the environment. Steindor et al. (2011) discovered a connection between tree bark acidity and SO<sub>2</sub> concentration local areas' air pollution. Bark acidity variations across samples may be attributed to locations (Poikolainen 2004). According to certain research, bark pH is crucial for assessing the impact of air pollution. It is advised to use tree bark as a sensitive and uncomplicated indication of air pollution. For instance, pollution from cities and steel factories has a significant negative impact on the Niepotomice Forest in southern Poland (Grodzinska 1971). Lower pH values are caused by sulfur dioxide concentrations (Steindor et al. 2011). According to Santamaria and Martin (1997), there is a direct association between the amount of SO<sub>2</sub> in the environment and the pH of tree bark, meaning that the acidity of the bark increases as SO<sub>2</sub> levels rise in the atmosphere.

Medium density fiberboard (MDF) is a product of the processing of products generated from bark (Xing et al. 2006). The mixed pH environment during resin curing is provided

(or generated) in large part by the acidity of the raw materials. To achieve the best bond strength, the press time and temperature must be modified for the pH environment. Acidity has a significant impact on how well PF resin cures. The reactivity of the resin functional groups decreased when the pH of the PF/particle system decreased (He and Riedl 2004). Additionally, due to their high extractive concentrations, all bark particles, whether treated or untreated, are more acidic than wood (Ngueho Yemele et al. 2008).

### Solubility of bark in cold and hot water

The solubility of *L. leucocephala* bark in cold water, hot water, and 1% NaOH is shown in Fig. 1. The maximum percentage of bark (41.36%) was soluble in alkali 1% NaOH, followed by hot water (14.45%) and cold water (11.06%). When compared to cold water, 1% NaOH's solubility was 30.3% greater, while hot water's solubility was 3.39%. This demonstrated how the solubility of bark was affected by variations in temperature and solvent.

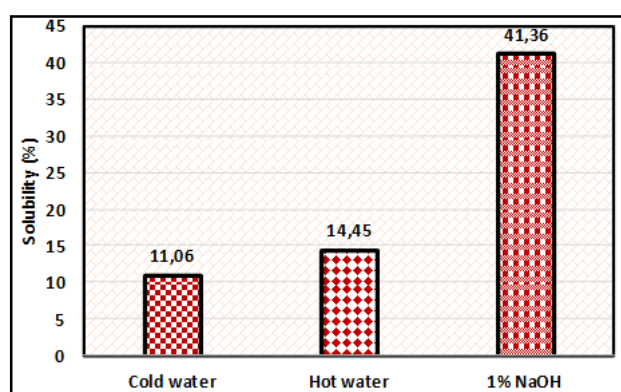


Fig. 1: Solubility of *L. leucocephala* bark.

The bark of *L. leucocephala* is soluble in cold water, as shown in Fig. 1. In comparison to hot water and 1% NaOH solubility, the solubility of *L. leucocephala* bark in cold water was the lowest (11.06%). Despite this, the cold-water solubility extracts indicate that the bark fraction is more important than the wood fraction (Hoong et al. 2011). Analysis of the bark of eucalyptus (*Eucalyptus globulus*) was performed to look for potential sources of antioxidant chemicals. The stem bark therefore exhibited greater antioxidant activity in terms of reducing power, peroxidation inhibition, and O<sub>2</sub> and DPPH radical scavenging capacity. It is well known that polyphenolic substances with extraordinary antioxidant properties, such as flavonoids, anthraquinones, anthocyanidins, and xanthenes, are frequently found in the plant family Leguminosae (Siddhuraju et al. 2002). The water and 2.5% Na<sub>2</sub>SO<sub>3</sub> extracts both exhibited high antioxidant activity.

Tannin extracts from the bark of the *A. mangium* tree were discovered to be highly concentrated in phenolic compounds and to have the ability to replace the traditional phenol-formaldehyde (PF) adhesive used in the plywood production sector. The plywood board was bonded using a tannin adhesive (tannin-paraformaldehyde) made from *A. mangium* bark tannin by cross-linking with paraformaldehyde. Although tannin adhesive was used, it was discovered that the resulting bonding strength was only appropriate for interior grade applications (Hoong et al. 2011).



Fig. 1 shows that the bark of *L. leucocephala* is soluble in hot water. Bark was 14.45% more soluble in hot water than in cold water (11.06%). This demonstrates how temperature influences bark solubility in the same media. Hot water is frequently used for bark extraction. Inorganic salts, smaller phenolic compounds, and carbohydrates can also be extracted using this technique. Therefore, a thorough characterization of bark extracts is necessary to comprehend their characteristics and limitations (Bianchi et al. 2015). This information indicates that *Pinus radiata* bark hot water extracts contain a high polyphenol content and robust antioxidant activity and that the amount of proanthocyanidin in each bark greatly affects the antiradical potency of hot water extracts. The primary components of HWE have been identified as flavonoids (taxifolin, nongallate catechin, quercetin), phenolic acids (proto-catechuic acid), and a significant quantity of proanthocyanidin, suggesting that it has the potential to be a powerful antioxidant (Ku and Mun 2007).

### **Solubility in 1% NaOH**

The solubility of *L. leucocephala* bark in 1% NaOH is shown in Fig. 1. In comparison to solubility in cold and hot water, the bark of *L. leucocephala* was the most soluble (41.36%). The increased hemicellulose and cellulose decay or degradation, which affects the strength and bonding of glue or materials, was caused by high alkaline solubility. The amount of 1% NaOH solubility (T-212), a measure of the amount of material that is easily degradable (such as parenchyma cells), was calculated from the milled material. It has been demonstrated that this value correlates with the amount of nonfiber material in the bark (De Meijer and van der Werf 1994).

Geng et al. 2006 found that at 175°C, strong binding to wood was generated by tannin extracted from pine bark with 1% NaOH at 100°C for 30 min (bark-liquor ratio of 1 g/5 mL). This finding suggests that the alkaline bark extract could be used as a wood glue. In addition, the fiberboards manufactured from alkaline-treated bark displayed lighter color, more internal bonding strength, greater modulus of rupture, and greater modulus of elasticity in contrast to the control panels (Geng et al. 2006). Even while alkaline treatment of wood weakens the lignin linkages between the cellulosic fibers and softens the fibers, it nevertheless produces less damaged and more flexible fibers after refinement, which is why it has been commercially employed to produce chemomechanical pulp (Zanuttini et al. 1998).

### **Chemical composition of bark**

The chemical composition of *Leucaena leucocephala* bark is depicted in Fig. 2. As can be observed, holocellulose comprises much of the composition (132.85%). Hemicellulose (103.66%) and alpha cellulose make up holocellulose (29.29%). Lignin made up 38.24% of the lignin in *L. leucocephala* bark, while ash and extractive made up the lowest amount.

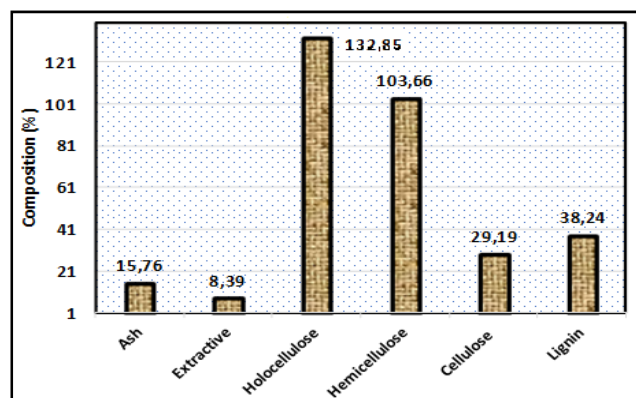


Fig. 2: *L. leucocephala* bark's chemical composition.

### Ash content of bark

The percentage of ash in the bark of *L. leucocephala* is shown in Fig. 2. According to the graph, 15.76% of *L. leucocephala* bark contained ash. A high ash content may impair the combustion process, reducing the materials' heating value and making them less attractive for fuel production. The ash concentration is widely recognized to be substantially higher in bark (Feng et al. 2014). The amount of bark and the amount of ash correlated linearly (Werkelin et al. 2005). Because the amount of bark increased with smaller diameters, there was a substantial correlation between the ash content and the diameter of the stem, branch, and twigs. As a result of its relationship to components such as sulfur, chlorine, and potassium that pose issues for combustion devices, particularly in terms of corrosion, the results of the correlation study demonstrate how crucial it is to monitor ash as a quality criterion (Toscano et al. 2013).

Ash content and extraction are two significant factors that have a direct impact on how efficient biomass fuels are as a source of heat. A plant part's appeal as fuel is decreased by a high ash concentration, but it is increased by a high extractive content (Demirbas 2002). Important factors directly influencing the heating value include ash and extractive content. A plant part's appeal as fuel is decreased by a high ash concentration, but it is increased by a high extractive content (Demirbas 2002). The silica concentration and overall ash content of the bark residues were both significantly increased by the presence of sand in the raw material (Ngueho Yemele et al. 2008).

### Bark extractive content

The extractive content of the bark of *L. leucocephala* is shown as a percentage in Fig. 2. The graph indicates that 8.39% of the bark of *L. leucocephala* was extracted. The high extractive concentration is due to the bark's acidity, which causes a decrease in pH. The processing during sawing, including stick saw blades and casing errors, may be impacted by the presence of extractives. Due to their high extractive contents, all bark particles, whether treated or untreated, are more acidic than wood (Ngueho Yemele et al. 2008). Environmental pollution also affects differences in the amounts of extractives and mineral substances in wood, bark, and roots (Krutul et al. 2014), with the content of extractives in bark being 13% greater at the butt-end, 36% higher in the middle, and 12% higher at the top of the trunk from unpolluted areas.

The amounts of phenolic extractives (acetone extractives) in wood were shown to be substantially linked with decay resistance (Gierlinger et al. 2004). The processing of larch wood may also be impacted by water-soluble extractives. During saw milling, arabinogalactans could become stuck in the blades, which could lead to inaccurate cutting and halts (Sairanen 1982). Therefore, from a wood machining perspective, progenies/provenances with larger quantities of water-soluble extractives would be less interesting.

### **Holocellulose content of bark**

The percentage of holocellulose present in the bark of *L. leucocephala* is shown in Fig. 2. According to the graph, the holocellulose content of the *L. leucocephala* bark was 132.85%. Increased holocellulose content may be caused by the polysaccharide's heat reaction during hydrolysis. Furthermore, pulp-worthy materials have a high holocellulose content.

Holocellulose is the entire polysaccharide fraction of wood, bark, and lignocellulosic material, which contains cellulose and all the hemicelluloses, after the extractives and the lignin are taken out of the original natural material. Bark's naturally higher phenolic concentration and wood's lower carbohydrate content are favorable for producing phenolic thermosetting resins (Duret et al. 2013). Polysaccharides can be hydrolyzed through thermal, chemical, or enzymatic processes (Matsushita et al. 2010). With longer reaction times and higher acid concentrations, the holocellulose content decreased because of polysaccharide hydrolysis (Duret et al. 2013).

The optimum conditions are primarily dependent on the holocellulose and Klason lignin content of the bark because of the condensation of phenolic components such tannins under acidic conditions and no extractive condensed tannins. Klason lignin bark, the hydrolyzed holocellulose and furfural contents of the response variation and reaction time had a substantial impact. The mass loss barely changed because of the reaction time. Long reaction times resulted in an increase in polysaccharide breakdown. Because holocellulose hydrolysis is increasing, reaction time effects are detrimental to the holocellulose content of bark (Xavier et al. 2012).

### **Hemicellulose content of bark**

Fig. 2 shows the hemicellulose content of *L. leucocephala* bark. *L. leucocephala* bark has a hemicellulose content of 103.66%. Hemicellulose frequently serves as a storehouse of food. Hemicellulose is closely related to pectin and is used as a transitional phase when lignin is made from pectic compounds. The total galacturonic acid concentration and degree of esterification in the pectin from bark with and without epidermis varied. The pectin solution from the bark without the epidermis had a higher consistency or perceived viscosity, indicating that it had a stronger gelation ability. This result is likely because contaminants were also removed at the same time as galacturonic acid during alcohol precipitation, and the pectin obtained from bark with epidermis had a lower overall galacturonic acid level. Therefore, pectin with varying levels of esterification may be found in the bark of mulberry branches (Liu et al. 2010). Biopolymers with branching polysaccharides make up the hemicellulose group (Kerr and Bailey 1934). The cellulose structure is simpler than theirs. The most unstable parts of biomass from a thermal perspective are hemicelluloses. As a result, hemicellulose degrades more quickly and at lower temperatures than cellulose and lignin.

### Cellulose content of bark

The percentage of cellulose present in the bark of *L. leucocephala* is shown in Fig. 2. The graph demonstrates that the bark of *L. leucocephala* contained 29.19% cellulose. Bark's cellulose content was lower than wood's cellulose content. The most prevalent organic substance on earth is cellulose, an organic component of the main cell wall of green plants having the chemical formula  $(C_6H_{10}O_5)_n$  because of its alluring chemical and physical characteristics, cellulose is a biomass resource that has been studied and used for many years and will continue to be a crucial raw material to produce paper, food, and additives for the optical and pharmaceutical sectors (de Souza Lima and Borsali 2004). In addition, a few nations have proposed cellulosic biomass for ethanol production (Sassner et al. 2008) as an alternative energy option to satisfy the demands.

### Lignin content of bark

*L. leucocephala* bark's lignin concentration was 38.24% (Fig. 2.). Bark has a higher lignin content than wood because lignin in biomass regulates the rate of reaction during combustion. A complex polymer of phenylpropanoid units known as lignin is created through the oxidative coupling of one to three different forms of hydroxycinnamic alcohols, which serve as the usual monolignol precursors. The polymer's equivalent aromatic units are H for 4-hydroxyphenyl, G for 3-methoxy-4-hydroxyphenyl, and S for 3,5-dimethoxy-4-hydroxyxyphenyl (Marques et al. 2006). The H/G/S ratios of the lignin are used to classify them. It is appropriate to remark that cinnamic acids can occasionally be present in substantial amounts in the lignin structure of bark and corks, given the chemistry of those materials (Ralph et al. 2004).

Lignin broke down for pyrolysis and had its char burned during the second stage. The pyrolysis rate increased for biomass that included more cellulose. However, slower pyrolysis rates were produced by biomass that included more lignin (Gani and Naruse 2007). When the lignin content increases, the overall reaction rate decreases. The lignin in biomass, as a result, regulates the reaction rate during burning. Since lignin primarily regulates the rate of breakdown during pyrolysis, the lignin content is chosen as a metric to correlate with the pyrolysis outcomes (Gani and Naruse 2007). Bark's Klason lignin content and furfural in solution both benefited from reaction time effects. Due to improved hydrolysis extraction of polysaccharides and soluble components, a reaction period of 24 hours enhanced the Klason lignin content of bark (Xavier et al. 2012).

## CONCLUSIONS

*Leucaena leucocephala*'s stem bark is thought to be the least acidic, which may be a result of less polluted surroundings and/or the extractive nature of the bark. Compared to hot and cold water, this species was most soluble in 1% NaOH. These findings revealed that the solubility of the stem bark of *L. leucocephala* was strongly impacted by temperature and various solvent types. The bark of *L. leucocephala* has a high ash concentration, making it less useful as fuel. This may have an impact on the combustion process, which impacts the thermal properties of the materials. The *L. leucocephala* bark extractive content is directly correlated with its acidity

and pH level. Despite hemicellulose's instability and faster and lower temperature of decomposition than cellulose and lignin, *L. leucocephala* bark's high holocellulose concentration makes it valuable for pulp production. The cellulose content of the bark was lower than the cellulose content of the wood, which is used as a raw material for the manufacture of paper, food, and additives in the optical and pharmaceutical industries. In addition, cellulosic biomass is proposed for ethanol production as an alternative energy option to satisfy the demands. The amount of lignin in the biomass, which is higher in the bark than in the wood, regulates the reaction rate during combustion. According to this investigation, the bark of *L. leucocephala* was less acidic. The high solubility of bark increases its potential as a source of carbohydrates, and the chemical makeup of bark affects pyrolysis's quick combustion.

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### REFERENCES

1. Ahmad, Z., Wee, L.S., Fauzi, M.A., 2011: Mechanical properties of wood-wool cement composite board manufactured using selected Malaysian fast grown timber species. *ASM Science Journal* 5(1): 27–35.
2. ASTM D110-84, 2001: Standard test method for ash in wood.
3. ASTM D1103, 1978: Method of test for alpha-cellulose in wood.
4. ASTM D1104, 1985: Method of test for holocellulose in wood.
5. ASTM D1105, 2001: Standard test method for extractive-free in wood.
6. ASTM D1106, 2001: Standard test method for acid-insoluble lignin of wood.
7. ASTM D1109, 2001: Standard test method for 1% sodium hydroxide solubility of wood.
8. ASTM D1110-84, 2001: Standard test method for water solubility of wood.
9. ASTM E70, 2019: Standard test method for pH of aqueous solutions with the glass electrode.
10. Bianchi, S., Krosiakova, I., Janzon, R., Mayer, I., Saake, B., Pichelin, F., 2015: Phytochemistry characterization of condensed tannins and carbohydrates in hot water bark extracts of European softwood species. *Phytochemistry* 120: 53–61.
11. Chow, P., Nakayama, F.S., Blahnik, B., Youngquist, J.A., Coffelt, T.A., 2008: Chemical constituents and physical properties of Guayule wood and bark. *Industrial Crops and Products* 28(3): 303–8.
12. Dalahmeh, S.S., Pell, M., Vinneras, B., Hylander, L.D., Oborn, I., Jonsson, H., 2012: Efficiency of bark, activated charcoal, foam and sand filters in reducing pollutants in gray water. *Water, Air, and Soil Pollution* 223(7): 3657–71.

13. De Meijer, E.P.M., Van Der Werf, H.M.G., 1994: Evaluation of current methods to estimate pulp yield of Hemp. *Industrial Crops and Products* 2: 111-120.
14. De Souza Lima, M.M., Borsali, R., 2004: Rodlike cellulose microcrystals: Structure, properties, and applications. *Macromolecular Rapid Communications* 25: 771-787.
15. Demirbas, A., 2002: Relationships between heating value and lignin, moisture, ash and extractive contents of biomass. *Fuels* 20(1): 105-111.
16. Duret, X., Fredon, E., Masson, E., Desharnais, L., Gerardin, P., 2013: Optimization of acid pretreatment to increase the phenolic content of *Picea abies* bark by surface response methodology. *Bioresource* 8(1): 1258-1273.
17. Eberhardt, T.L., Reed, K.G., 2006: Strategies for improving the performance of plywood adhesive mix fillers from southern yellow pine bark. *Forest Products Journal* 56(10): 64-8.
18. Feng, S., Cheng, S., Yuan, Z., Leitch, M., Xu, C., 2013: Valorization of bark for chemicals and materials: A review. *Renewable and Sustainable Energy Reviews* 26: 560-578.
19. Feng, S., Yuan, Z., Leitch, M., Charles, C., 2014: Hydrothermal liquefaction of barks into biocrude. Effects of species and ash content/composition. *Fuel* 116: 214-220.
20. Gani, A., Naruse, I., 2007: Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomasses. *Renewable Energy* 32(4): 649-661.
21. Geng, X., Zhang, S.Y., Deng, J., 2006: Alkaline treatment of black spruce bark for the manufacture of binderless fiberboard. *Journal of Wood Chemistry and Technology* 26: 313-324.
22. Gierlinger, N., Jacques, D., Schwanninger, M., Wimmer, R., Paques, L.E., 2004: Heartwood extractives and lignin content of different larch species (*Larix* sp.) and relationships to brown rot decay resistance. *Trees* 18(2): 230-236.
23. Grodzinska, K., 1971: Acidification of tree bark as a measure of air pollution in southern Poland. *Bulletin of the Polish Academy of Sciences: Biomedical Engineering and Biotechnology* 19(3): 189-195.
24. He, G., Riedl, B., 2004: Curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrates. *Wood Science Technology* 38(1): 69-81.
25. Hoong, Y., Paridah, T., Feng, Y., Jalaluddin, H., Chuah, L.A. 2011: International Journal of Adhesion & Adhesives A new source of natural adhesive: *Acacia mangium* bark extracts copolymerized with phenol formaldehyde (PF) for bonding Mempisang (*Annonaceae* spp.) veneers. *International Journal of Adhesion and Adhesives* 31(3): 164-167.
26. Kerr, T., Bailey, I.W., 1934: The cambium and its derivative tissues. X. Structure, optical properties, and chemical composition of the so-called middle lamella. *Journal of Arnold Arboretum* 15: 327-349.
27. Kim, K.H., Tucker, M., Nguyen, Q., 2005: Conversion of bark rich biomass mixture into fermentable sugar by two stages dilute acid-catalyzed hydrolysis. *Bioresource Technology* 96: 1249-1255.
28. Krutul, D., Zielenkiewicz, T., Zawadzki, J., Radomski, A., Antczak, A., Drozddek, M., 2014: Influence of urban environment originated heavy metal pollution on the extractives and mineral substances content in bark and wood of oak (*Quercus robur* L.). *Wood Research* 59(1): 177-190.

29. Ku, C.S., Mun, S.P., 2007: Characterization of proanthocyanidin in hot water extract isolated from *Pinus radiata* bark. *Wood Science and Technology* 41(3): 235–247.
30. Liu, L., Cao, J., Huang, J., Cai, Y., Yao, J., 2010: Extraction of pectin with different degrees of esterification from mulberry branch bark. *Bioresource Technology* 101(9): 3268–3273.
31. Marques, A.V., Pereira, H., Rodrigues, J., Meier, D., Faix, O., 2006: Isolation and comparative characterization of a Bjorkman from the saponified cork of Douglas-fir bark. *Journal of Analytical and Applied Pyrolysis* 77: 169–176.
32. Matsushita, Y., Yamauchi, K., Takabe, K., Awan, T., Yoshinaga, A., Kato, M., Kobayashi, T., Asada, T., Furujo, A., Fukushima, K., 2010: Enzymatic saccharification of *Eucalyptus* bark using hydrothermal pretreatment with carbon dioxide, *Bioresource Technology* 101: 4936–4939.
33. Ngueho Yemele, M.C., Koubaa, A., Niokhor Diouf, P., Blanchet, P., Cloutier, A., Stevanovic, T., 2008: Effects of hot-water treatment of black spruce and trembling aspen bark raw material on the physical and mechanical properties of bark particleboard. *Wood and Fiber Science* 40(3): 339–351.
34. Pereira, H., Graca, J., Rodrigues, J.C., 2003: Wood chemistry in relation to quality. In: Barnett JR, Jeronimidis G (Eds.) *Wood Quality and Its Biological Basis* vol. 3. CRC Press, Blackwell Publishing, Oxford, (3): 53–83.
35. Poikolainen, J., 2004: Mosses, epiphytic lichens, and tree bark as bio monitors for air pollutants – specifically for heavy metals in regional surveys. Oulu University Press: Oulu, 64 p.
36. Ralph, J., Lundquist, K., Brunow, G., Lu, F., Kim, H.P.F., Schatz, P.F., Marita, J.M., Hatfield, R.D., Ralph, S.A., Christensen, J.H., Boerjan, W., 2004: Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids. *Phytochemistry Review* 3(1-2): 29–60.
37. Sairanen, P., 1982: Properties and usages of larch in the mechanical forest industry in Soviet Union. *Metsäntutkimuslaitoksen tiedonantoja*, 72 p. (In Finnish).
38. Santamaria, J.M., Martin, A., 1997: Tree bark as a bioindicator of air pollution in Navarra, Spain. *Water, Air, and Soil Pollution* 98(3-4): 381–387.
39. Sassner, P., Galbe, M., Zacchi, G., 2008: Techno-economic evaluation of bioethanol production from three different lignocellulosic materials. *Biomass and Bioenergy* 32: 422–430.
40. Siddhuraju, P., Mohan, P.S., Becker, K. 2002: Studies on the antioxidant activity of Indian Laburnum (*Cassia fistula* L.): A preliminary assessment of crude extracts from stem bark, leaves, flowers, and fruit pulp. *Food Chemistry* 79(1): 61–67.
41. Steindor, K., Palowski, B., Goras, P., Nadgorska-Socha, A., 2011: Assessment of bark reaction of select tree species as an indicator of acid gaseous pollution. *Polish Journal of Environmental Studies* 20(3): 619–622.
42. Takano, T., Murakami, T., Kamitakahara, H., Nakatsubo, F., 2008: Formaldehyde adsorption by Karamatsu (*Larix leptolepis*) bark. *Journal of Wood Science* 54: 332–336.

43. Toscano, G., Riva, G., Pedretti, E. F., Corinaldesi, F., Mengarelli, C., Duca, D., 2013: Investigation on wood pellet quality and relationship between ash content and the most important chemical elements. *Biomass and Bioenergy* 56(0): 317–322.
44. Werkelin, J., Skrifvars, B.J., Hupa, M., 2005: Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest 29: 451–466.
45. Xavier, D., Emmanuel, F., Philippe, G., Eric, M., 2012: Spruce bark hydrolysis to optimize phenolic content. *Cellulose Chemistry and Technology* 46(9-10): 541-550.
46. Xing, C., Deng, J., Zhang, S.Y., Rield, B., Cloutier, A., 2006: Impact of bark content on the properties of medium density fiberboard (MDF) in four species grown in eastern Canada. *Forest Products Journal* 56(3): 64–69.
47. Zanuttini, M., Citroni, M., Martinez, M.J., Marzocchi, V., 1998: Chemimechanical pulping of poplar wood. Alkaline wood pretreatment at low temperature. *Holzforschung* 52(4): 405–409.

RAFIDAH MD SALIM\*, JAHIMIN ASIK, MOHD SANI SARJADI, LIEW KANG CHIANG  
UNIVERSITY OF MALAYSIA SABAH  
FACULTY OF TROPICAL FORESTRY  
UMS ROAD, 88400  
KOTA KINABALU, SABAH  
MALAYSIA

\*Corresponding author: rafidahs@ums.edu.my