Contact angle of modified fibrovascular bundle of salacca (Salacca sumatrana Becc.) frond by NaOH + Na$_2$SO$_3$ combination

L Hakim$^{1,2,*}$, R Widyorini$^1$, W D Nugroho$^3$, T A Prayitno$^3$ and Y S Lubis$^4$

$^1$Department of Forest Product Technology, Faculty of Forestry, Universitas Sumatera Utara, Jl. Tri Dharma Ujung No. 1 Kampus USU, Padang Bulan, Medan 20155, Indonesia.
$^2$JATI-Sumatran Study Analysis Center, Faculty of Forestry, Universitas Sumatera Utara, Jl. Tri Dharma Ujung No. 1 Kampus USU, Padang Bulan, Medan 20155, Indonesia.
$^3$Department of Forest Product Technology, Faculty of Forestry, Universitas Gadjah Mada, Jl. Agro No. 1, Yogyakarta 55281, Indonesia.
$^4$Research and Development Agency of Forest Fibers Technology, Ministry of Environment and Forestry, Jl. Raya Riau-Bangkinang Km.9, Kuok-Bangkinang, Kampar 28294, Indonesia.

*E-mail: luthfi@usu.ac.id.

Abstract. The fibrovascular bundle (FVB) of the salacca frond is one of the potential raw materials in the development of bio-composite technology. The purpose of this study was to investigate the wettability of FVB using the contact angle method after the alkali modification treatment. The method of this research was to use FVB frond of Salacca sumatrana Becc. which was treated with alkaline modification of the combination of NaOH+Na$_2$SO$_3$ at various concentrations. The results showed that the combination of NaOH 1M+Na$_2$SO$_3$ 0.4 M had the smallest contact angle, which means that the FVB has a good wettability value compared to the control treatment. Based on the results, it can be concluded that the modification of NaOH+Na$_2$SO$_3$ can increase the wettability of FVB.

1. Introduction
Salak sidempuan (Salacca sumatrana Becc.) is one of palm tree cultivated by agroforestry system in the Tapanuli Selatan District, Sumatera Utara Province, Indonesia. Salak sidempuan palm tree not only produced an edible fruit, but also it produced an abundant of fibrovascular bundle (FVB) in frond part. Fibrovascular bundle is a cell tissue in monocots plants that contain of fibers, xylem, phloem and axial parenchyma which bind to one another to form bundles. Geometrically, fibrovascular bundles has the same shape with natural fibers such as jute, kenaf, sisal, choir, abaca, pineapple leaves, and others (Hakim et al., 2019; Zhai et al., 2013).

Salacca frond has potential as a raw material for the manufacture of composite boards (Widyorini et al., 2018; Widyorini et al., 2019). However, FVB frond has several weaknesses, including the surface properties which still contains contaminant (lot of wax, parenchyma and other impurity deposits) that will make it difficult to spread the adhesive. One way to remove impurities is to carry out surface chemical modification treatments. Alkaline chemical modification has been done by many
previous studies (Darmanto et al., 2017; Kundu et al., 2018; Ourhim et al., 2018). However, the modification using the combination of NaOH+Na$_2$SO$_3$ on FVB frond of S. sumatrana has never been reported previously, especially to determine the wettability level of FVB.

Evaluation of the wettability of surface by the contact angle can be helpful for predicting compatibility between raw materials and adhesive. Hubbe et al., (2015) stated the contact angle can be the key quality of adhesion. The investigation of contact angle of the modified FVB will determine the performance of adhesion of composite board manufactured from modified FVB frond of S. sumatrana. Based on the background, the purpose of this study was to investigate changes in the contact angle of FVB due to alkaline modification of the NaOH+Na2SO3 combination.

2. Materials and Methods

2.1. Materials
The frond of S. sumatrana were obtained from community plants in Tapanuli Selatan District, Sumatera Utara Province, Indonesia. The frond was picked when it was around 15-20 years old. The NaOH (sodium hydroxide anhydrate 96%) and Na$_2$SO$_3$ (sodium sulfite anhydrate 98%) were used for the alkali treatment of FVB obtained from Merck (Darmstadt, Germany). The leaf was removed from the main frond after harvesting, and the fronds were cut 100 cm in length. The fronds were immersed in water for 4 (four) weeks to soften them and make it easier to separate the FVB from the frond tissue. The fibrovascular bundles were separated from the frond with an iron comb after being soaked. Figure 1 illustrates the stages of obtaining a fibrovascular bundle.

![Figure 1](image)

**Figure 1.** Stages of obtaining a fibrovascular bundles; (A) plants; (B) frond harvesting; (C) frond immersion; (D) fibrovascular bundles, respectively.

2.2. Alkali treatment
Fibrovascular bundles were immersed with eight different solutions of chemical modification under room condition and without pressure (Table 1). The fibrovascular bundles were removed from the solution and rinsed with cold water (20 $\pm$ 3 $^\circ$C) before being air dried. The moisture content of FVB is air dry condition prior to contact angle testing.

| Treatment | NaOH concentration (Mol) | Na$_2$SO$_3$ concentration (Mol) | time (minutes) |
|-----------|--------------------------|-------------------------------|---------------|
| A (control) | 0% | 0% | 30 |
| B (control) | 0% | 0% | 60 |
| C | 1% | 0% | 30 |
| D | 1% | 0% | 60 |
| E | 1% | 0,2% | 30 |
| F | 1% | 0,2% | 60 |
| G | 1% | 0,4% | 30 |
| H | 1% | 0,4% | 60 |
2.3. Contact angle measurement
The contact angle was measurement using Schellbach et al., (2016) methods (Figure 2). Two fibers are attached to the sample holder and placed under the microscope. The distance between the parallel fibers was 1-2 mm. Water was dripped between the two fibers to obtain a liquid that hangs between the two FVBs. The water droplet image was photographed using a stereo optical camera facility. The image was analyzed using IC-Measure version 2.0.0.245 software to measure the contact angle of the FVB. Measurements were made at 4 angles formed between the FVB and the liquid in contact with the FVB and averaged.

![Figure 2](image)

**Figure 2.** Contact angle measurement based on Shellbach et al. (2016) methods
a: diameter of fibrovascular bundle; b: liquid (water); c: distance between FVB’s; d: water meniscus; $\Theta$: contact angle water to fibrovascular bundle; and e: curvature of the meniscus formed by water.

3. Result and Discussion
The contact angle is defined as the angle formed between the normal lines of solid and liquid surfaces drawn from the intersection between 3 phases, namely liquid, solid and gas (Van de Velde and Kiekens, 1999; 2000; Kose et al., 2018). The contact angle is measured to determine the level of wettability of the fibrovascular bundle against the liquid (water) in order to determine whether or not a substance is wetting it easily. The contact angle photograph of modified FVB of *S. sumatrana* frond has shown at Figure 3.

![Figure 3](image)

**Figure 3.** Contact angle of modified FVB of *S. sumatrana* frond
The best value of contact angle is the treatment of NaOH 1M+Na₂SO₃ 0.4M for 60 minutes immersion (25.35°). This value is much lower than the contact angle of bamboo, jute, ramie, and kenaf which has a contact angle value above 60° (Fuentes et al., 2011; Chen et al., 2013; Ishak et al., 2014). Changes in the contact angle of water occur due to changes in chemical composition and surface roughness during alkali modification (Chowdhury et al., 2013; Chen et al., 2018). Modification of NaOH and the combination of NaOH+Na₂SO₃ made the contact angle decreased compared to the water immersion treatment. Table 2 describe that the contact angle between water treatment and modification shows a decreasing change in the contact angle.

| Treatment and time of immersion | Contact angle (°) |
|--------------------------------|-------------------|
| A: water for 30 min             | 100.45            |
| B: water for 60 min             | 83.56             |
| C: NaOH 1M for 30 min           | 55.48             |
| D: NaOH 1M for 60 min           | 53.44             |
| E: NaOH 1M+Na₂SO₃ 0.2M for 30 min| 36.02             |
| F: NaOH 1M+Na₂SO₃ 0.2M for 60 min| 34.39             |
| G: NaOH 1M+Na₂SO₃ 0.4M for 30 min| 25.49             |
| H: NaOH 1M+Na₂SO₃ 0.4M for 60 min| 25.35             |

The treatment of NaOH+Na₂SO₃ at low concentrations is very effective in reducing the contact angle. Some of the amorphous hemicellulose components were degraded during NaOH and combination of NaOH+Na₂SO₃ treatment which caused by the FVB surface roughness to increase due to the appearance twisting, microfibril, and the loss of some impurities and wax as discussed in the changes of the FVB surface morphology (Cai et al., 2016). Surface changes due to degradation and accessibility of hydroxyl groups on the FVB surface are two factors that affect the level of wettability (Chowdhury et al., 2013; Sinha et al., 2017).

4. Conclusions
The chemical modification treatment of the NaOH+Na₂SO₃ combination was effective in reducing the FVB contact angle. Reducing the contact angle will increase the FVB wettability which it will facilitate to spreading adhesive on the FVB surface.

Acknowledgement
The authors thank to Bapak Ady Suhendra Harahap dan Bapak Ronni Oktorio (salak farmer in Persalakan Village, Tapanuli Selatan District, Sumatera Utara Province, Indonesia) for supplying fibrovascular bundle of salacca frond.

References
[1] Cai M, Takagi H, Nakagaito A N, Li Y and Waterhouse G I N 2016 Composites-Part A: Applied Science and Manufacturing 90 589
[2] Chen H, Cheng H, Jiang Z, Qin D, Yu Y, Tian G, Lu F, Fei B and Wang G 2013 Bio Resources 8 2827
[3] Chen H, Zhang W, Wang X, Wang H, Wu Y, Zhong T and Fei B 2018 J Wood Sci 64 398
[4] Chowdhury M N K, Beg M D H, Khan M R and Mina M F 2013 Cellulose 20 1477
[5] Darmanto S, Rochardjo H S B, Jamasri and Widyorini R 2017 AIP Conference Proceedings 1788 030060.
[6] Fuentes C A, Trana L Q N, Dupont-Gillain C, Vanderlindden W, Feyter S D, Vuurea A W V and Verpoest I 2011 Colloids and surfaces A physicochem Eng Aspects 288 89
[7] Hakim L, Widyorini R, Nugroho W D and Prayitno T A 2019 Bio Resources 14 7943
[8] Hubbe M A, Gardner D J and She W 2015 Bioresources 10 8857
[9] Ishak Z A M, Ariawan D, Salim M S, Taib R M, Thirmizir A and Phua Y J 2014 *ECCM16 - 16TH European conference on composite materials* (Spain: Seville)

[10] Kose R, Utsumi M, Yatsui H, Tun-Abdul-Aziz M K and Okayama T 2018 *J Trop For Sci* **30** 546

[11] Kundu S P, Chakraborty S, Majumder S B and Adhikari B 2018 *Construction and Building Materials* **174** 330

[12] Ouarhima W, Essabira H, Bensalah M O, Zaria N, Bouhfida R and Qaiss A 2018 *Composites Part B* **154** 128

[13] Schellbach S L, Monteiro S N and Drelich J W 2016 *Mater Letters* **164** 599

[14] Sinha A K, Narang H K and Bhattacharya S 2017 *International Conference on Advancements in Aeromechanical Materials for Manufacturing (ICAAMM-2016)* Materials Today Proceedings **4** 8993

[15] Van de Velde K and Kiekens P 1999 *Die Angewdante Makromolekulare Chemie* **272** 87

[16] Van de Velde K and Kiekens P 2000 *Indian J fiber & textile Res* **25** 8

[17] Widyorini R, Umemura K, Septiano A, Soraya D K, Dewi G K and Nugroho W D 2018 *BioResources* **13** 8662

[18] Widyorini R, Umemura K, Soraya D K, Dewi G K and Nugroho W D 2019 *BioResources* **14** 4171