RESEARCH ARTICLE

TANNINS AND CATECHINS CONTENT OF GAMBIER (UNCARIA GAMBIER ROXB) IN RELATION WITH ADHESIVE QUALITIES AND BONDING STRENGTH OF COLD SETTING GLUE

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Abstract

This research aims to know the quality of the various production centers gambier in West Sumatra and the main constituent component (tannins and catechins) in relationships with the bonding strength of adhesive gambier. This research using an exploratory method with three replications. Sampling took from five production centers in West Sumatra namely in the Lima Puluh Kota District covering Muaro Paiti, Pangkalan, and Sago Halaba. While in the Pesisir Selatan District include Batang Kapeh and Siguntur. The sampling method is done randomly by taking Gambier at the place of production of one of the Nagari. The results showed a strong relationship between the high content of tannin Gambier with adhesive strength is generated in the amount of $R^2 = 0.9032$. The higher tannin content of, the adhesion force is generated will be higher, otherwise higher content of catechins which causes the lower adhesion strength. The best adhesion strength was Sago Halaban with the adhesive strength of 21.1 kg/cm², tannin content of 30.55%, catechin content of 44.47%. The adhesive quality produced from Gambier suitable the SNI 06-4565-1998, SII 0778-83 Adhesive Phenol Formaldehyde Liquid standards and suitable with Japanese Industrial Standart (JIS A 5908;2003)

Introduction:-

Gambier is an extract of the leaves and twigs of the gambier (Uncaria gambier Roxb) plant that produced by using hot water then precipitated, drained, molded and dried. Extraction process performed by manual compression and by using a hydraulic clamp (Kasim, 2011). The main chemical component of gambir is catechin and tannin. According to Fengel and Wegener, (1995) catechin is a monomer of tannins. If 3 to 8 molecules of tannin create a polymer, then the polymer will be classified as tannins condensation.

Tannin is an important component of plants. The extract of tannin has been widely used as tanning agents, inks, textile dyestuffs, and adhesives. According to Cartet, F. L., (1978) tannins have been widely used as the exterior type of wood adhesives. In addition, it provides good quality gluing results and low formaldehyde emissions (green technology and green products)(Kim, 2009)

The wood adhesive contains three main aspects that must be considered. All factors affect the quality of the adhesive. First, an aspect of given material including structure and anatomy of wood (cell arrangement, the direction of the fiber),

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physical properties (density, water content, flowers shrink, porosity, wettability), chemical properties (a chemical constituent of cells, extractive). Second, aspects of adhesive including the type, nature and the use of adhesive and forming components including additional material. Third, the aspect of gluing technology including preparation of adhesive (composition and method kneading), compression, adhesive spread, working conditions (duration, temperature, a method of implementation) (Prayitno, 1996)

Cold setting glue could be made from the raw material of tannin in gambier that can be hardened at low temperature in a relatively short time. To achieve the properties cold setting glue in gambier, it is required conversion into derivates by sulfitation process. The research Kasim (2011) showed that the production of solid wood adhesives can harden at room temperature and perform the process sulfitation in the solution of gambier by adding sulfite. The produced adhesive quality is strongly influenced by the quality of gambier. The diversity of gambier quality produced by farmers will lead to the variety of all the quality of the produced adhesive. Depend on the case, it is needed a research about “Tannins and Catechins Content of Gambier (Uncaria gambier Roxb) in Relation with Glue Qualities and Bonding Strength of Cold Setting Glue. By knowing the tannins and catechins content, it can be predicted that the suitability of gambier will be used as an adhesive raw material.

Material and Methods:

Material and Equipment:
The material used in this study are a sample of gambier that randomly taken from five production areas. Gambier in the form of a tube with a hard texture. The reduced in size to gambier flour escapes 80 mesh, and chemicals used such as NaHSO₃, NaOH, ethyl acetate, NaCl by Merck, gelatin, indigo, alcohol and filter paper.

Equipment needed in this study are: ultrasonic bath, spectrophotometer UV, analytical balance, blender, desiccators, oven, usual funnel, pipette 2 ml, 10 ml, and 50 ml, burette, hot plate, Petri dish, a flask of 50 ml and 500 ml, beaker of 100 ml, watch glass, stoppered 100 ml Erlenmeyer flask, vacuum pump, furnace, such aluminium, porcelain dish, aluminium foil, rod stirrer, wood size of 5 cm x 5 cm, Freiberg hide powder from Germany and Universal Testing Machine type Galdabini 1990.

Research Design:
The research used the exploratory method with 3 replications. Gambier of each production center was expected to have different content of tannin and catechin.

Gambier was obtained from the following regions: Muaro Paiti, Sago Halaban, Batang Kapeh, Siguntur, and Pangkalan.

Analysis of Gambier:
Determination of the quality of gambier includes analysis of water content by the method ASTM D2974, tannin content by Gravimetry used Freiberg hide powder from Germany and catechin content by SNI 01-3391-2000 method, insolubility water, and alcohol content by SNI 01-2891-1992 method.

Gambier Adhesive Production:
Gambier adhesive formulation was 45 grams of gambier (dry weight), 6 grams of NaHSO₃, 100 ml of water, 10% hexamethylenetetramine (HE) and NaOH as needed until it reached pH 10. NaHSO₃ is dissolved in water, gambier and performed sulfitation at 100 °C for 2 hours. Then the solution was cooled down and added NaOH, added HE as much as 10% of the dry weight of gambier while stirring for 3 minutes.

Gluing Wood Process:
1. In this study, the gluing wood process was carried out in the order of gluing, cold pressing, conditioning, and bonding strength testing. The procedures of gluing wood as follows;
2. 5 x 5 cm of wood samples for 15 pairs were prepared
3. The Adhesive was spread on one side of each pair with a size 4 cm x 5 cm (according to the direction of the fibers)
4. Other wood samples were placed with a contact area of 4 cm x 5 cm (according to the direction of the fibers)
5. Conditioned for 5-minute
6. Cold pressed and conditioned for a week before testing
7. Bonding strength was tested
Physical and Mechanical Testing:-
Physical properties of adhesive covers the viscosity, gelatinization time, specific gravity, solid content, acidity, adhesive appearance, all physical used JIS A 5908:2003 (Association) and Mechanical Testing (German Standard 1980)

Statistical Analysis:-
The relationship between tannins and catechins content with adhesive quality was regression analysis. The contains of observation from the quality of gambier are showed in tables and analyzed descriptively. A result of tannin content (x) associated with the quality of adhesion (y) and then the conclusion has taken. The next chart content of catechins (x) associated with the quality of adhesion (y) and finally the conclusion is made.

Result and Discussion:-
Raw Materials Gambier:-
Analysis of the materials of Gambier included analysis of water content, ash content, tannin content, catechin content, insoluble water content, and insoluble alcohol content. Gambier was ground with a mortal to refine of gambier and sieved 80 mesh.

Analysis of Gambier:-
Based on Table 1, the water content of gambier from five regions showed a fairly homogeneous number with a range of 13.81% to 16.04% when compared with Kasim et al. (2015) study that the water content of gambier in some samples ranged from 12.87% to 17.53%. Water quality 1 of gambier is a maximum of 14% and water quality 2 is maximum of 16%. Gambier MuaroPaiti and Pangkalan are according to quality 1, Gambier Sago Halaban and Siguntur are according to quality 2.

The higher water content materials, the amount of raw material (dry weight) which used to be more and more needed. Determination of water content is taken to know the gambier quality. Gambier is also very important to use as a reference for determining the dry weight basis of the material to be used in the sulfitation (Kasim 2011)

The ash content in Table 2 displays various data. Based on SNI 01-3391-2000, the quality of gambier is 1 and 2 is a maximum of 5%. Gambier Pangkalan has not according to standard. According to Sudarmadjiet. al., (1989) ash is an inorganic substance remaining from the combustion of an organic material. The value of ash content is closely related to the mineral content contained in a material, purity, cleanliness of a product produced and whether the treatment process is good or not.

The content of the inner ash of gambier is caused by two things, namely minerals in plants and minerals carried by non-gambier materials that are considered to be deliberately added by farmers (Kasim, 2011)

Based on Table 1, the catechins content in gambier ranged from 44.47% to 62.18%. BatangKapeh and Siguntur are classified as a quality of 1, MuaroPaiti, Pangkalan is classified as a quality of 2. In research the content of catechins ranged from 14.76% to 54.97%. The results of Taniguchi et al. (2007) found that from 31 gambier samples collected from gambier traders in 4 countries, Japan, Indonesia, Singapore, and China, it was known that catechin content ranged from 0.17 g to 0.76 g per 1 g sample with the average of 0.43g / g or 43%.
At gambier in Indonesian, the catechin content ranged from 22%-76% with an average of 51.76%.

**Table 1**: Analysis of Gambier (%)

| Gambier       | Water Content ± SD | Ash Content ± SD | Catechin Content ± SD | Tannin Content ± SD | Insoluble Water Content ± SD | Insoluble Alkohol Content ± SD |
|---------------|--------------------|------------------|-----------------------|---------------------|------------------------------|-------------------------------|
| Muaro Paiti   | 13.81±1.02         | 2.83±0.30        | 59.75±3.67            | 30.31±4.27          | 3.16±1.15                    | 3.25±0.42                     |
| Sago Halaban  | 15.91±0.26         | 2.11±0.35        | 44.47±3.16            | 30.55±4.39          | 3.36±1.02                    | 3.11±0.63                     |
| Batang Kapeh  | 16.04±0.63         | 2.05±0.21        | 62.18±2.35            | 29.69±3.96          | 3.46±0.41                    | 3.10±0.24                     |
| Pangkalan     | 13.30±0.53         | 13.16±0.70       | 55.37±2.70            | 23.78±2.79          | 3.22±1.30                    | 3.15±0.78                     |
| Siguntur      | 14.56±0.69         | 3.74±0.32        | 60.33±1.65            | 18.26±2.79          | 3.36±0.70                    | 3.34±0.32                     |

The catechin content in each of the gambier production areas is influenced by the condition of the extracted leaves. Young gambier leaves contain catechins and extract yields are higher than old leaves. Handling of extraction leaves also affects the levels of gambier catechins such as the delay of gambier leaves for two days which affects the decrease in catechin content and the yield of gambier twigs and leaves extraction process.

The tannin content obtained was from 18.26% to 30.55%. The highest tannin content in the gambier Sago Halaban and the lowest in the gambier Siguntur. The tannin contained in gambier can be extracted to obtain tannin products that have a high purity content. The process of taking tannins in gambier random involves the separation process between catechin and tannin compounds, both of them are polyphenol compounds. Tannins have properties that can dissolve in alcohol and cold water. Tannin compounds can dissolve in water and the better the solubility in hot water so that when testing it is expected that all tannins can dissolve, but it is suspected that they will also dissolve non-tannin compounds together. This must be avoided because it will cause interference in the adhesive process (Kasim, 2011).

The presence of mixing or impurities in gambier will reduce the content of tannins, catechins and aromas contained in gambier which are absolute requirements that must be met by gambier with good quality and for export (Denian, 2004). Testing of water-insoluble material content was carried out to determine the amount of non-tannin ingredients contained in Gambier.

Based on SNI 01-3391-2000 the content of the water is insoluble and the alcohol is insoluble up to 7% for quality 1 and 10% for quality 2. From the Table, the content of the ingredients is insoluble water ranges from 3.16% to 3.46%. Alcohol-insoluble material content ranged from 3.10% to 3.34%. Water-insoluble material content indicates the number of impurities contained in Gambier. The presence of mixing or impurities in gambier will reduce the content of tannins, catechins and aroma contained in gambier which are absolute requirements that must be met by gambier with good quality and for export (Denian, 2004). Testing of water-insoluble material content was carried out to determine the amount of non-tannin ingredients contained in Gambier.

**Qualities of Cold Setting Glue Adhesive:**

Gambier which has been carried out by the sulfitation process is the basic material for making an adhesive called resin. Into the resin, hexamethylenetetraamine added it as a hardener so that it becomes an adhesive. Table 2 show adhesive viscosity ranging from 128 cPs to 640 cPs. According to JIS A 5908:2003, the viscosity at 30 °C of ±100 cPs.

The specific gravity of the adhesive depends on the polymerization of tannin content in Gambier. The more perfect the polymerization level forms a bond between the flavonoid components, the greater the polymer will be formed and the higher the specific gravity of the adhesive. According to JIS A 5908:2003, specific gravity at 30 °C is 1.228-1.235 g/cm³. The solids content is very influential on adhesive quality. The higher the level of adhesive solids, the higher the resin content. This resin level gives an indication of whether or not the adhesive is produced.
Table 2:-Quality of Cold Setting Glue Adhesive

| Gambier         | Viscosity (cps) | Specific Gravity | Solid Content (%) | Gelatinization Time (mnt) | Acidity (pH) | Appearance       |
|-----------------|-----------------|------------------|-------------------|---------------------------|--------------|------------------|
| Muaro Paiti     | 345             | 1.2617           | 34.36             | 40                        | 10.1         | Solid Black      |
| Sago Halaban    | 152             | 1.2035           | 33.86             | 60                        | 10.2         | Blackish Brown   |
| Batang Kapeh    | 640             | 1.2642           | 33.61             | 40                        | 10.2         | Solid Black      |
| Pangkalan       | 128             | 1.2552           | 36.56             | 50                        | 10           | Blackish Brown   |
| Siguntur        | 144             | 1.2550           | 34.48             | 40                        | 10.5         | Blackish Brown   |

Vick, (1999) states that the maximum bonding bond can occur if the adhesive moistens all wood surfaces as a bonded material so that contact between adhesive molecules and wood molecules can occur so that the intermolecular attraction between wood and adhesive can bind well. Then the increase in solid content will improve the quality of the adhesive. Solids content according to JIS A 5908:2003 are 50 -58%.

Adhesive gelatinization takes place at a temperature of 100 °C (boiling water) so that the adhesive polymerization process takes place very quickly. The length of time the gelatinization of the adhesive will affect the life pot of the adhesive. Adhesive pot life can be used as a guideline for using adhesives in plywood and particle board industries. The adhesive gelatinization time in the study ranged from 40 minutes to 70 minutes and according to JIS A 5908:2003, the gel time is 50-70 minutes.

The appearance of adhesive in all gambier production centers is not much different, because the adhesive gambier pH gambier. The color appearance is also influenced by the initial conditions of the raw material and the adhesive pH. In some production centers, the gambier produced is black while in some other production centers it is brown.

Relation of Gambier's Tanin, Catechin Content, and Adhesive Strength:-

The relation between tanin content and gambier catechins with adhesive Strength can be seen in Table 3. High tanin content in gambier causes the polymerization reaction to take place perfectly when reacted with sulfite salts in a medium of water at high temperatures (Kasim, 2011). The strength of Cold Setting Glue adhesive is very impactful on the tanin content and also affects the quality of the adhesive.

Seen in the Table, the highest strength is found in the gambier Sago Halaban with the tannin content of 30.55%. The lowest strength is found in gambier Siguntur with the tannin content of 18.26%. When viewed from the research data, gambier in the northern region (Lima Puluh Kota) tends to have high tannin levels, while gambier in the southern region (Pesisir Selatan) tends to contain high levels of catechins.

To determine the relationship between gambier quality parameters consist of tannin and catechin content of gambier on the quality of adhesive used regression analysis. From this regression analysis, it will be seen the relationship between tannins and catechins with the strenght of the adhesive produced as Figure 2 and 3.

Table 3:-Tannin, Catechin and Adhesive Strength

| Region of Sample | Tannin Content (%) | Catechin Content (%) | Strength (kg/cm²) |
|------------------|--------------------|----------------------|-------------------|
| Muaro Paiti      | 30.31              | 59.75                | 19.45             |
| Sago Halaban     | 30.55              | 44.47                | 21.1              |
| Batang Kapeh     | 29.69              | 62.18                | 17.25             |
| Pangkalan        | 23.78              | 55.37                | 15.25             |
| Siguntur         | 18.26              | 60.33                | 11.5              |

The results of the regression calculation showed that there was a relationship between tannin contents and the resulting strength adhesive of R²: 0.9032. Based on the literature, the high tannin content produces high strength because of the perfect polymerization in the presence of tannins and hexamethylene tetraamine as a bridge connecting the polymerization.

As a natural material, many factors influence the chemical composition of gambier so that the results obtained have a low relationship. Among them, there are water content, ash and other ingredients which are intentionally or
unintentionally added to affect and are thought to inhibit the polymerization reaction.

The results of regression calculations showed that there was no relationship between catechin gambier content and the stickiness that was produced which was indicated by the value of $R^2 = 0.3054$. Catechins which are non-binding monomers to form polymers are thought to produce low strength. Gambier catechins cannot be used as a determining parameter for the Strength of solid wood adhesives. The catechins in gambier undergo crystallization in the process of water evaporation. The catechins in gambier are not a similar component but a mixture of various isomers.

![Relationship Tannin and Adhesive Strength](image1)

**Figure 2:** Relationship Tannin and Adhesive Strength

![Relationship Catechin and Adhesive Strength](image2)

**Figure 3:** Relationship Catechin and Adhesive Strength

**Conclusions:**
The catechin content of gambier samples ranged from 44.47 to 62.18, samples from the Sago Halaban area did not, according to SNI 01-3391-2000, while the gambier tannin content ranged from 18.26 to 30.55%. Gambier tannin content has a close relationship with the bonding strength produced, which is $R^2 = 0.9032$. The higher of tannin content is related to the bond strength, meanwhile the higher of catechin content makes the bond to be lower.

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