Utilization Of Kraft-Lignin From Black Liquor Waste Extraction As An Agent To Improve The Quality Of Physical Properties Of Fine Paper

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Abstract. Lignin is one of the constituent component of wood, but the presence of lignin can be a nuisance in the paper making process. Lignin will reduce the physical and optical properties of paper. The objective of this study is to determine the advantages of lignin-kraft and its impact to modify cationic starch on the physical properties of fine paper. The study was conducted in steps. In the first step extraction was carried out to obtain the kraft-lignin, by using two extraction methods that is acid extraction with thermal and acid extraction with centrifuge. Kraft-lignin was tested from both methods, the optimum test value will be continued at the cooking stage into resin-lignin. Resin-lignin will be a modified compound with level addition 3% and 6% of the dry weight of cationic starch, then it will be applied to the handsheet with 13 variation, namely blank; DS existing (2 Kg/TP, 4 Kg/Tp, dan 6 Kg/TP), cationic starch emulsion + resin-lignin 6%, cationic starch substitution + resin-lignin 3%, and cationic starch substitution + resin-lignin 6%. Variation of cationic starch substitution + resin-lignin 6% at level addition 6 Kg/TP indicates the best value of physical strength. Especially on tensile strength, wet tensile strength, bursting, tearing, dan internal bonding value.

1. Introduction
Lignin specifically creates a barrier to enzymatic attack while the crystal structure is very insoluble in water, so hemicellulose and lignin produce a protective sheath around cellulose. (Stenius, 2000). The pulping process is the process of obtaining cellulose extract from biomass raw materials, usually wood. Kraft process is one method of pulping using sodium hydroxide (NaOH) and sodium sulfide (Na₂S) solutions. The solution will result in the breakdown of the lignin molecule into a smaller segment because there is a sodium yag salt dissolved in the cooking liquid. Black liquor is a remnant of pulping fluid which generally consists of 14-18% solids which is commonly known as weak black liquor (WBL) with a pH of 12 or more.

About 65% of the solids contained in black liquor are organic compounds derived from wood such as lignin, resins and fatty acids, acids from carbohydrates, and other organic compounds; The remaining 35% is inorganic, white liquor which is used in pulping processes such as Na₂CO₃, Na₂SO₄, Na₂S, Na₂S₂O₃, NaOH and NaCl. The lignin content found in black liquor is generally used by the pulp and paper industry to be an energy source using boilers and regenerating other inorganic content so that it can be reused in the pulping process through the clinical cycle. Holladay (2007: 53) states that black with a concentration of 40-50% solids and then burned to a value of getting heat of about 12,000 to 13,000 BTU / ounce dry weight. Kraft lignin, also called sulfate or alkali lignin, is obtained
from black liquor by the extraction method using an acid hydrolysis process, so that pure lignin-kraft compounds can be obtained which can be further utilized in various industrial activities.

2. Research Methodology
The method used in this study is literature study and practice. From the material and knowledge found in journals and related sources. The first stage of the study was extraction of weak black liquor samples by two different methods that is the comparison of two Lignin-kraft extraction methods with the acid hydrolysis process with thermal assistance (heating temperature) and a gradual centrifuge. By suspending salt in water and minimizing pH with sulfuric acid, a fine lignin deposit is obtained according to the equation: 

\[ 2R-Ona + H_2SO_4 \rightarrow 2ROH \downarrow + Na_2SO_4 \]  

(Li Jinjing, 2011). Then the extraction results were tested using the AIR and ASL checking method based on TAPPI T222 om-98 and Biorefinery Test Methods L 1: 2016; metal content checking using ICP; FT-IR and SEM testing to compare the similarity of test results with the literature. Then the lignin extract with the most optimum value is cooked into resin-lignin and then added to the cooking cationic starch low DS as much as 3% and 6 of the dry weight of the starch to be used in the process of making a handsheet. Starch modification of temperature, viscosity, and value of the load was done using PCD. Then the application is carried out on the handsheet. After obtaining complete data, then the data is processed using a comparison with the existing literature.

2.1 Tools and Materials
The material used in this experiment is Weak Black Liquor (WBL) from PM mill which results in cooking 100% Acacia crasi carpa with the process using a kraft process; H_2SO_4 10% and 20%; 5% NaOH, pure water.

The tools used are Glass Beaker Glass (150 ml, 300 ml, 500 ml, 1000 ml), Centrifuge Tubes, pH Meters, Ovens (60o c and 40 oC), Hot Plate with automated stirer da magnet, Analytical Balance, Thermometer, Pipette Drops, Tube titration, Aluminum Foil, Spatula, Auto Clave, Glass Fiber Filter, Spectrometer, FTIR, ICP, SEM.

2.2 Research Procedure

2.2.1 Black Liquor Content
Testing of black liquor produced based on TAPPI Test Method T 625 cm - 85 and TAPPI Test Methode T 650 OM - 99.

2.2.2 Acid Hydrolysis Extraction Method I with Thermal
In this method, lignin deposits are obtained by adding 20% sulfuric acid as sediment.

2.2.3 Acid Hydrolysis Extraction Method II with Centrifuge
In this method, lignin deposition and washing processes occur repeatedly.

2.2.4 Identification of Lignin Content
The purpose of this stage is to test whether the lignin content contained in lignin-kraft is maintained / not damaged during the extraction / manufacturing stage. The steps for identifying lignin follow the TAPPI T222 om-98 and Biorefinery Test Methods L 1: 2016.

2.2.5 ICP Testing
Before metal content testing using ICP, lignin is prepared into a test solution first. The results are awaited until the test results are complete.

2.2.6 Identification of Lignin using FTIR and SEM
For this stage, the author sent samples of extracted lignin-kraft to the laboratory at the Bandung Institute of Technology for FTIR and SEM testing.
3. Result and Discussion
3.1 The results of lignin extraction

From the graph of acid soluble lignin (ASL) and acid insoluble residue (AIR) test results, L1 shows the results of thermal extraction and L2 shows the results of centrifuge extraction. The results can be obtained that the extraction method using centrifuge gives the value of lignin which is more and more stable than the thermal method. This happens because the addition of heat can accelerate the extraction process that occurs but degrades more lignin content contained in the sample.

Testing the remaining metal content shows the value of the levels of metals and elements that are very low and can be tolerated for further research processes. However, high Na content is obtained, this is indicated by the Na content contained in the cooking solution (NaOH and Na2S) binds to the extracted lignin and will not cause interference in the subsequent process because in resin synthesis it is necessary to add more Na to dissolve lignin.

From the reading of the FT-IR spectrum in the two results of lignin extraction it was found a similarity at the base of the compiler with the FTIR spectrum reading from the literature. The results of the second reading of lignin extract in the spectrum of region II are quite different from the results of the literature, this is indicated by the number of unstable triple bond terminations from the sample source in the extraction process. Then in region IV there are some impurities originating from the black leachate source used.
SEM test results show a striking difference from the surface structure of lignin at magnification of 10 μm. The surface of lignin by thermal method looks lumpy and uneven compared to lignin by centrifuge method. Then the SEM EDS results show that the element C content in lignin from centrifuge results is higher, this will greatly affect the effectiveness of the OH exchange reaction with the carboxylate group to improve the physical properties of the paper next.

3.2 Modified starch testing

From the starch quality testing, the following results were obtained:

| Type Of Sample | pH (25 °C) | Viscosity (cP) |
|----------------|------------|----------------|
|                |            | 65 °C  | 55 °C  | 45 °C  | 35 °C  | 25 °C  |
| Cationic low DS existing | 7.0 | 16  | 210 | 280 | 330 | 350 |
| emulsion 3% | 7.3 | 36.8 | 42 | 71 | 84 | 120 |
| Emulsion 6% | 7.5 | - | - | 13 | 30.40 | 51.60 |

In the results of testing the viscosity value, the effectiveness of using resin-lignin is seen to reduce and maintain the viscosity value of the cationic starch. With the addition of 6% resin-lignin sustainability, the viscosity of the load can decrease by 85.43% from the blank at 25 °C. This shows the use of resin-lignin with the use of small doses can reduce the use of steam and the use of compound stabilizers to maintain the value of the viscosity of the starch in the application on paper machines.

| Load Starch (PCD) | Testing |
|-------------------|---------|
| Cationic starch   | mV(1)  | Ueq/L(1) | mV(2) | Ueq/L(2) |
| +315              | 501.7  | +306     | 484.1 |

| emulsion starch + cationic resin-lignin 3% | mV(1) | Ueq/L(1) | mV(2) | Ueq/L(2) |
| +336 | 540.3 | +345 | 553.1 |

| emulsion starch + cationic resin-lignin 6% | mV(1) | Ueq/L(1) | mV(2) | Ueq/L(2) |
| +369 | 683.8 | +358 | 646.9 |

From the load test results, cationic starch added with resin-lignin showed an increase in load of 30.05 mV on the addition of cationic starch + resin-lignin 3% emulsion and 53 mV at 6%. The increase in
cationic starch loading value increases with the added dose of resin-lignin. This occurs because the OH chain exchanges in the starch making group and is replaced by a hydroxymethyl group (-CH₂OH) carried by resin lignin. Substitution of this group causes the possibility of forming bonds between starch, fibers, fillers, and other materials used in the papermaking process to be more optimal. This increase in charge is one indicator of the modification of the physical and chemical properties of the starch used. This will later play a role in the cross-environmental process of making paper. So that the lignin produced can be an alternative material that is cheap and easy to obtain.

3.3 Testing the physical properties of the handsheet
After testing the strength of the paper on the handsheet with 13 variations, namely:

1: Blank
2: DS existing
3: 6% emulsion
4: substitution 3%
5: substitution 6%

Testing the physical properties of the paper from the overall variation shows the superiority of using cationic starch 6% with a dose of 6 kg / TP, a decrease in bulky value of 5.57%; an increase in the tensile index value of 10.81; wet tensile index of 253.57%; and tear index of 7.73% of the blank.

Handsheet checking on bursting and internal bonding values, used variations:

1: Blank
2: emulsion 6%
3: substitution 3%
4: substitution 6%
5: DS existing

In the bursting and internal bonding tests, the cationic starch + resin-lignin 6% substitution was not effective in producing paper strength values exceeding the effect obtained from the use of existing DS at doses of 2 and 4 kg / Tp. However, at a dose of 6 kg / TP it was seen an increase and showed the most optimal value of paper strength that was equal to 11.93% for the bursting index value and 48.61% for the internal bonding index value. From testing the physical properties of paper, the wet tensile, bursting, and internal bonding values show the performance of starch modification in forming bonds in web fabric, both between cationic starch molecules, fibers, and fillers contained in paper making. Then color testing is done on paper.

In testing the optical properties, the results show that the more additions of resin-lignin used to modify starch will reduce the degree of optical value of the paper produced.

4. Conclusion
Utilization of lignin-kraft yang is an extract from black liquor using acid extraction methods with a centrifuge giving results the most optimum and approaching results from existing literature in order to be able used as a cross-linking agent cheap and easy to get in the process of making paper.

Overall physical properties testing paper, namely bulky, tensile, wet tensile, tearing, bursting, and internal bonding show the most results the most optimum in variations use of cationic starch + substitution resin-lignin 6% at a dose of 6 kg / TP. This result is likely to increase with additional doses, so use of cationic starch can streamlined.

Occur impairment of optical properties in handsheets, on the L* value, whiteness, and brightness.

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