

Comparison study of lignin-kraft extraction process from black liquor using centrifuge and thermal acid hydrolysis methods

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Abstract. Black liquor is a remnant of pulping fluid which generally consists of 14-18 percent solids which is commonly known as weak black liquor (WBL) with a pH of 12 or more. About 65 percent 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 35percent percent is white liquor which is used in the pulping process. 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 kraft lignin compounds can be obtained which can be further utilized in various industrial activities. This study is comparing two kraft lignin extraction methods of acid hydrolysis process with thermal assistance (heating temperature) and a gradual centrifuge. The experiment results showed that the levels of lignin contained in black liquor consist of total calories of 391 kcal / Kg which can be processed into energy sources in the recovery boiler unit in further process. The result of kraft lignin extraction process using the acid hydrolysis method with gradual centrifuge stage is better than the thermal acid hydrolysis method. Quantitatively calculated with ASL values difference of around 0.002 mg / g of both the method and the AIR Value using centrifuge give an average yield of 969.815 mg / g, while using thermal assistance gives an average yield of 679.790 mg / g. Qualitatively, the centrifuge method is more optimal compared to the thermal method shown by the results of ICP, FTIR and SEM testing.

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. The pulping process is the process of obtaining cellulose extract from biomass raw materials, usually wood [1]. 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 percent solids which is commonly known as weak black liquor (wbl) with a pH of 12 or more. About 65 percent 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 percent 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



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an energy source using boilers and regenerating other inorganic content so that it can be reused in the pulping process through the clinical cycle [2]. States that black with a concentration of 40-50 percent solids and then burned to a value of getting heat of about 12,000 to 13,000 BTU / ounce dry weight [3]. 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 kraft lignin compounds can be obtained which can be further utilized in various industrial activities [4].

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 authors conducted a comparison of two Kraft lignin extraction methods with the acid hydrolysis process with thermal assistance (heating temperature) and a gradual centrifuge.

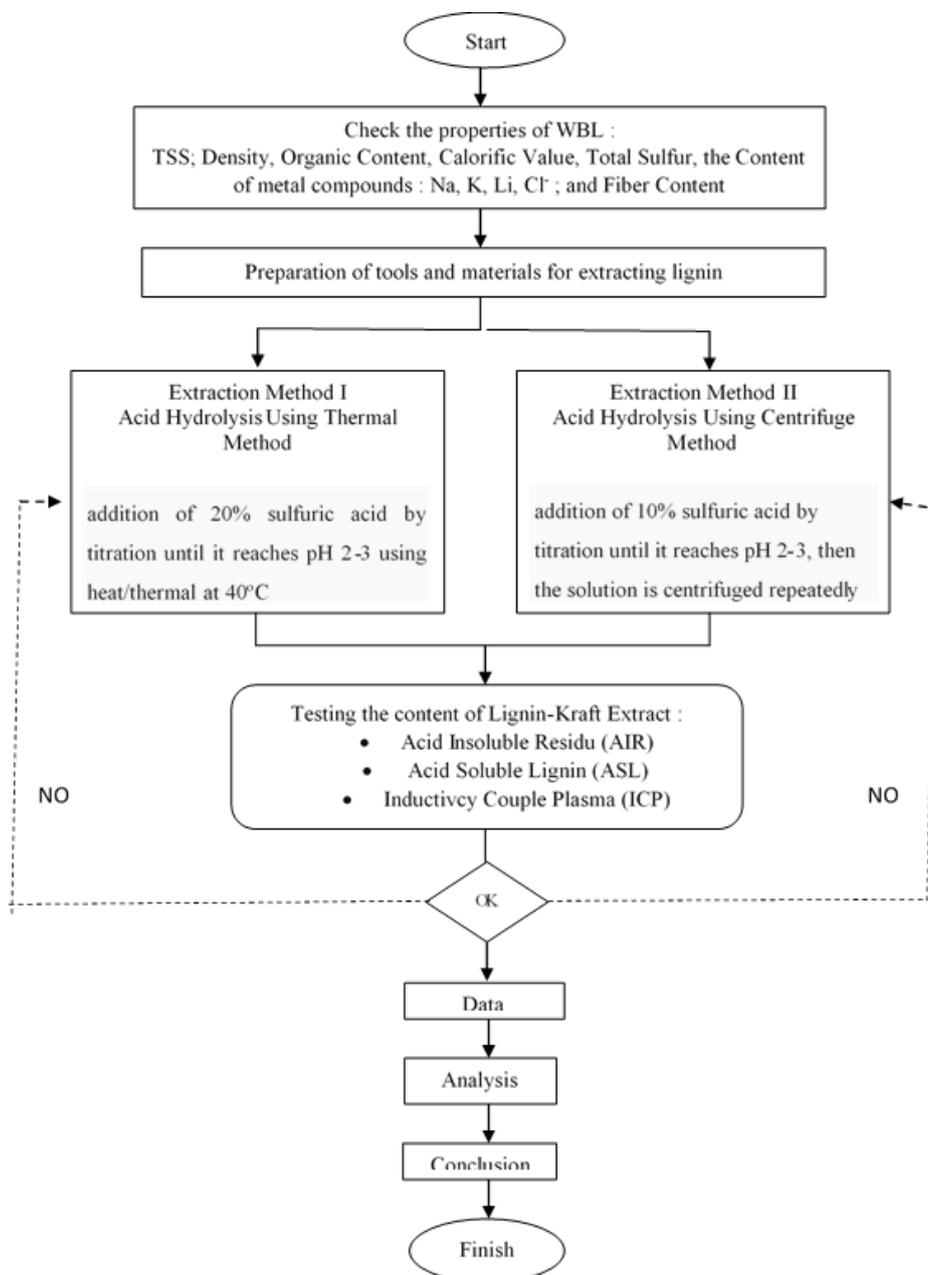


Figure 1. Research Flow Chart

2.1 Tools and materials

The material used in this experiment is weak black liquor (wbl) from pm mill which results in cooking 100 percent *Acacia crasi carpa* with the process using a kraft process; H₂SO₄ 10 percent and 20 percent; 5 percent NaOH, pure water.

The tools used are glass beaker glass (150 ml, 300 ml, 500 ml, 1000 ml), centrifuge tubes, ph meters, ovens (60° c and 40 °c), hot plate with automated stirrer and 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 method t 650 om - 99.

2.2.2 Acid hydrolysis extraction method I with thermal

In this method, lignin deposits are obtained by adding 20 percent sulfuric acid as sediment. The stages of this method are:

- 1) The wbl sample is filtered using fiber glass so that impurity contaminants can be separated from the liquid. To speed up the screening process is carried out with the help of vacuum.
- 2) The hot plate was heated, then a 1000 ml beaker filled with water was placed on the hot plate to make the environment similar to the water bath principle. The temperature is controlled to a constant at 40 °C.
- 3) While waiting for a constant temperature, WBL is placed on a 500 ml beaker glass, then 20percent sulfuric acid is added slowly with a titration tube until it reaches pH 2-3.
- 4) After pH is reached, the beaker glass is placed on the hot plate for 30 minutes with constant stirring using a magnetic stirrer.
- 5) Then the sample is filtered using fiber glass filters. The filtered residue is washed with pure water three times. To speed up the screening process, the sample has been diluted with water heated to a temperature of 30 °C.
- 6) The sample residue was placed on a cup coated with aluminum foil, then placed in an oven at 40 °C for 24 hours.
- 7) The dried sample is smoothed using a mortar until the powder is obtained with a uniform size

2.2.3 Acid hydrolysis extraction method II with centrifuge

In this method, lignin deposition and washing processes occur repeatedly. The process is:

- 1) The wbl sample obtained was filtered using glass filter so that impurity contaminants could be separated from the liquid. To speed up the screening process is carried out with the help of vacuum.
- 2) The filtered sample is added 10 percent H₂SO₄ slowly using the titration tube until it reaches a pH below 2.
- 3) Then the WBL is inserted into a centrifuge tube, then rotated at a speed of 4200 rpm for 5 minutes.
- 4) After that the lignin settles on the bottom of the tube separated by the liquid that is at the top.
- 5) 5percent NaOH is added to lignin deposits to get lignin dissolution, then filtered with fiber glass filters.
- 6) After lignin liquor is obtained. Then the sample was deposited again with 10percent H₂SO₄ to pH less than 2.

- 7) Then the sample is centrifuged again at a speed of 4200 rpm for 5 minutes.
- 8) Lignin deposits are obtained, then the sample is washed with distilled water. Then the sample is filtered
- 9) The sample is dried in an oven at a temperature of 50-60 °C for 24 hours
- 10) Lignosulfonate is obtained, then crushed with mortar to obtain a uniform size mixture.

2.2.4 Identification of lignin content

The purpose of this stage is to test whether the lignin content contained in kraft lignin 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 [5]. Then lignin levels can be calculated:

- Acid Insoluble residue (AIR) $AIR = \frac{m}{M} \times 1000 \text{ mg/g}$
- Acid soluble lignin (ASL) $ASL = \frac{A \times D \times V}{a \times b \times M} \times 1000 \text{ mg/g}$
- Total lignin = AIR + ASL

note:

m: OD residual filtrate; M: OD sample; A: spectrometer reading at 205 nm;

D: dilution factor; V: volume of filtrate (L); a: extinction coefficient of lignin (110 g / l based on TAPPI UM 250 nm); b: cuvette length (10 mm)

2.2.5 ICP Testing

Before metal content testing using ICP, lignin is prepared into a test solution first. The steps are samples weighed as much as 5 ± 0.5 gr, then placed in a 250 ml elemeyer tube. In the tube added 30 ml nitric acid PE, then the tube is placed on a hot plate with a temperature of 50 °C for 15 minutes until the sample is dried to eliminate the organic compounds contained therein. Then 10 ml percolate acid is added to the tube slowly to avoid the explosive impact that occurs. After that, the sample is diluted with pure water to 250 ml then stirred evenly. Place the sample in the sample storage tube for ICP checking and then label it. 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 kraft lignin to the laboratory at the Bandung Institute of Technology for ftir and sem testing.

3. Results and discussion

3.1 Black Liquor Content

Black liquor which was used in the present study was entirely derived from the results of cooking *Acacia crasi carpa* woods using the kraft process.

From the results above it can be concluded that cooking chemicals found in black leachate are quite high, and therefore a simple method is needed that can separate lignin from these chemical compounds without destroying the overall structure of lignin. The lignin value contained in black liquor can be read from the total caloric value contained, which is equal to 391 kcal / Kg which will then be processed into a source of energy (generally in most pulp industries) in the recovery boiler unit.

Table 1. Black liquor content

Parameter	Amount
Total solids	11.83 percent of the total liquid
Specific gravity	1.076 g/m ³
The content of organic compounds	67.68 Kg/Ton
The total active alkali in Na ₂ O	28.62 Kg/Ton
Total calories	391 kkal/Kg
Elemental content of Na	2.79 percent
Elemental content of K	0.30 percent
Elemental content of Li	28.8 ppm
Elemental content of Cl ⁻	0.14 percent
The amount of fiber	5.6 ppm

3.2 Identification of kraft lignin compounds

3.2.1 Results of Calculation of Lignin Levels with ASL and AIR

Lignin obtained will be formed into kraft lignin, because it comes from black liquor so that complex compounds are obtained, namely C₉H₁₀O₂.C₁₀H₁₂O₃.C₁₁H₁₄O₄. ASL is the result of the value of lignin which does not dissolve through the extraction process using concentrated acid (H₂SO₄), while AIR is the value of lignin which dissolves in the extraction process using acid.

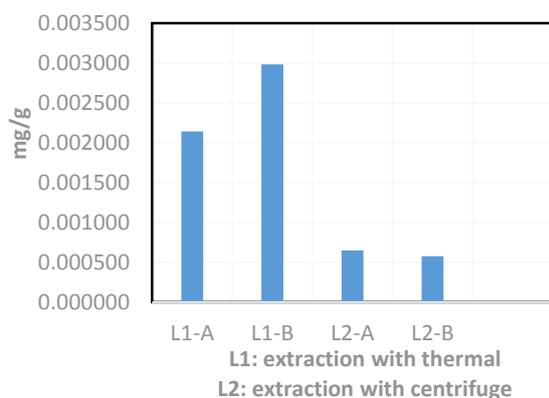


Figure 2. Content of *acid soluble residu* (ASL)

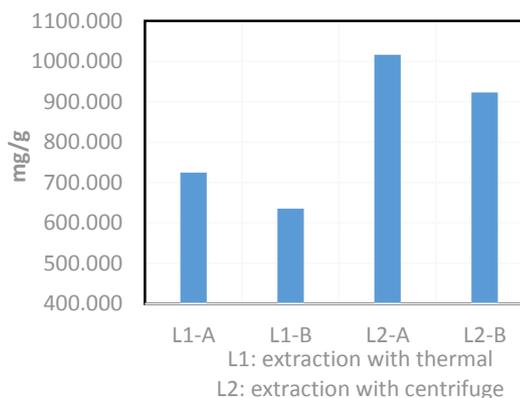


Figure 3. Content of *acid insoluable residu*

The value of lignin content using a centrifuge aid gives an average yield of 969,815 mg / g. While the value of lignin content using thermal assistance gives an average yield of 679,790 mg / g.

Table 2. Total Lignin Content

Sample	AIR (mg/g)	ASL (mg/g)	Total lignin content(mg/g)
1. Extraction using thermal I	739.34	0.002	739.342
2. Extraction using thermal II	635.09	0.003	635.093
3. Extraction using centrifuge I	1016.42	0.0006	1016.4206
4. Extraction using centrifuge II	923.20	0.0005	923.2005

The ash value difference of around 0.002 mg / g shows the extraction method with the help of a more optimum centrifuge to produce kraft lignin with a not too large solubility. Likewise with the ash value, around 400 mg / g between the two methods shows that the extraction method with the help of a centrifuge gives a more optimal result of contraction compared to thermal assistance. This is because with the help of a centrifuge it will help the reaction between black liquor and sulfuric acid, but it does not damage the existing lignin structure compared to the thermal extraction method. The function of the centrifuge here gives more possibility of contact time between black liquor and sulfuric acid.

3.2.2 The content of metal compounds by ICP testing

The value of metal compounds in kraft lignin is known through icp (inductively coupled plasma) testing. The purpose of checking this metal content is to compare the content of compounds that are still contained in the extraction results. The following is the value of the metal content contained in the kraft lignin,

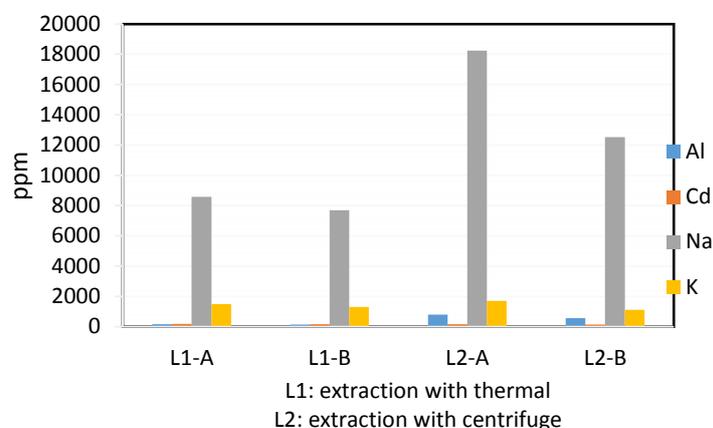


Figure 4. The content of metal compounds Al, Cd, Na, dan K in Kraft Lignin

The metal content contained in the kraft lignin with two extraction methods carried out showed uniform results in both repetitions (A and B). The highest metal content is in Na and K metals, this is due to the cooking process using NaOH and Na₂S solvents so that the metal content of Na is present in large amounts in black liquor and extracted lignin by the centrifuge and thermal methods.

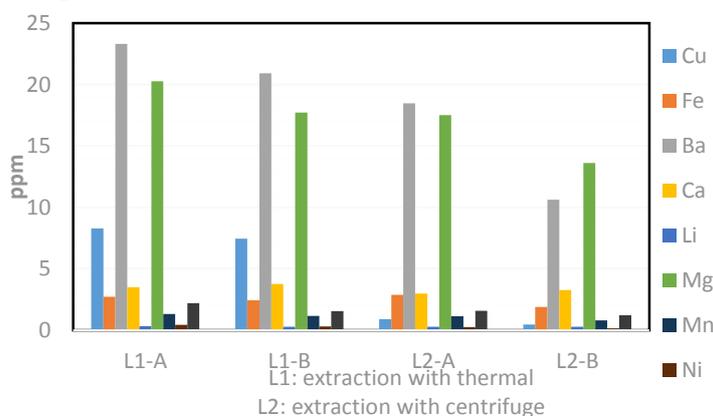


Figure 5. The content of metal compounds Cu, Fe, Ba, Ca, Li, Mg, Mn, Ni, dan Zn in Kraft Lignin

The content of Cu, Fe, Ba, Ca, Li, Mg, Mn, Ni, and Zn does not show a significant value because the overall results are very small, which is less than 25 ppm. Besides that, for Ag, Co, Cr, and Pb metal content it cannot be detected because the content is not found in the kraft lignin.

3.2.3 FTIR test results on Kraft-Lignin

The ft-ir test on these lignins aims to determine the compatibility of the kraft lignin spectrum adapted from the journal [6] with kraft lignin obtained through extraction with thermal assistance and centrifuge assistance. The spectrum obtained is as follows,

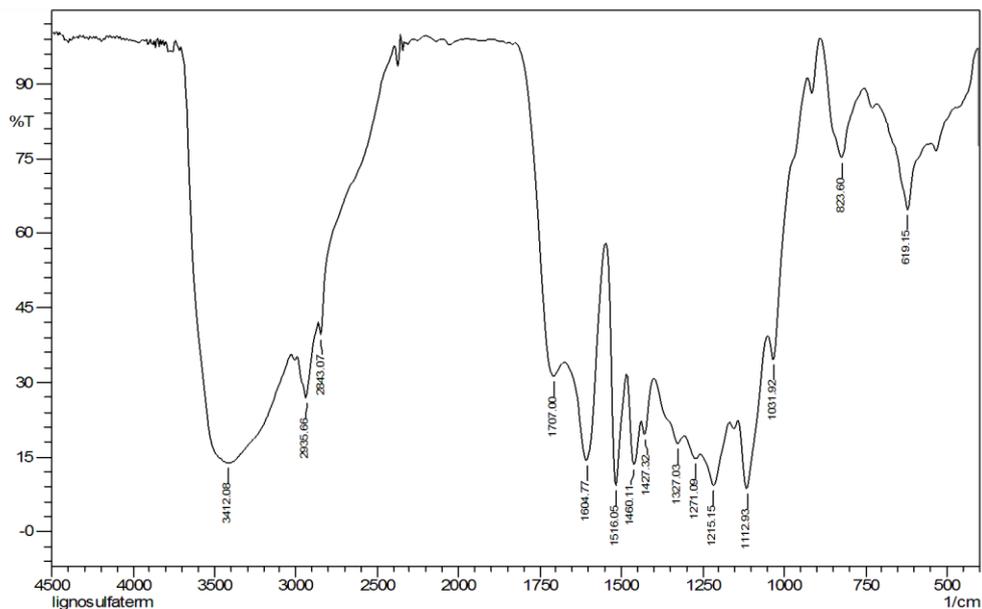


Figure 6. Spectrum of FTIR sample kraft lignin with thermal

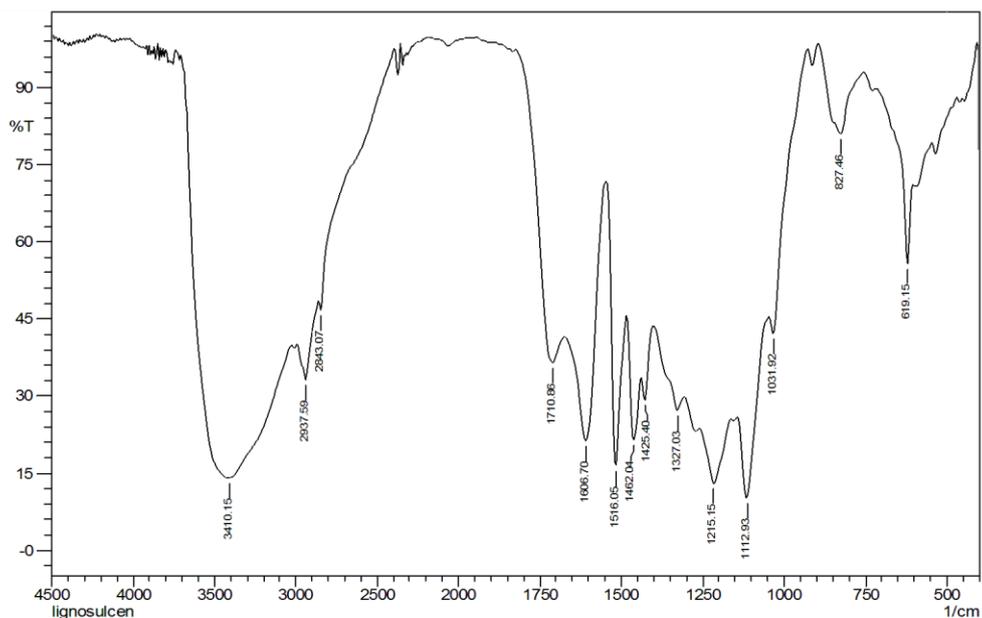


Figure 7. Spectrum of FTIR sample kraft lignin with

The results of the kraft lignin test with the help of heat obtained readings in region I (in regions with a frequency range of 4000-2000) there are types of compounds with a single OH oblation group that are quite large at the frequency of 3412.66, then 2 types of compounds with alkane types are also found (CH) at frequencies of 2935.66 and 2843.07. In region II with a range of 2500-2000 there were no recorded compounds that could be identified. In region III with a range of 2000-1500 there are many types of reading found for a compound C = O there is a frequency of 1707.00; 1604,77; 1460,11 and 1516,05 which may be indicated as esters. In region IV with a range of 1500-500 types of readings for nitro aromatic compounds (C-NO₂) at frequencies 1427.32 and 1327.03; ether compounds (C-O-C) on frequencies 1215,15, 1112,93, and 1031,92; Alkene compounds (C = C) are strong at a frequency of 823.60. In addition, also found the type of compound that has not been identified at a wavelength of 619.15 nm. The apparent difference from the two spectra above is that in the kraft lignin extract with the thermal method there are types of compounds that have not been identified at a wavelength of 619.15 nm with a higher frequency so that the thermal content of the extraction process is more than extraction. use a gradual centrifuge.

3.2.4 Result of SEM test

Scanning Electron Miscroscopy (sem) is one type of material characterization method to find out the microstructure of a material with a magnification of up to 150,000 times. Sem is usually equipped with EDS to capture X-rays reflected by electrons. The kraft lignin extract from the extraction process using the acid hydrolysis method uses repeated thermal and centrifuging of black liquor to form blackish brown powder solids. Qualitatively, the kraft lignin extract can be tested using SEM. The results of SEM testing can be seen in the picture below.

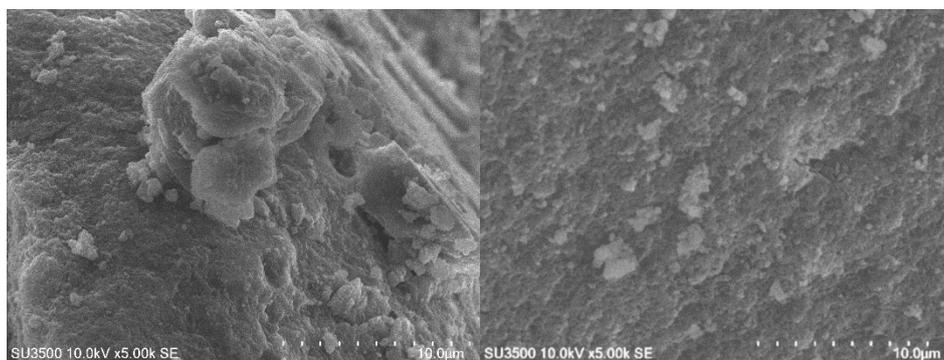


Figure 8. Result of SEM Testing sample kraft lignin with thermal

Figure 9. Result of SEM Testing sample kraft lignin with centrifuge

The SEM test results from the two images above show that the kraft lignin sample using a thermal method formed a grain texture that was not uniform compared to the results of the sem test in the kraft lignin sample using repeated centrifuge. Sem-eds can be used to analyze semi cumulative elements of the material. Sem-eds testing is one step in the analysis of deposits (impurities) contained in Kraft lignin extract. The results of sem-eds showed that the element C content in the sample of kraft lignin extract with the centrifuge method obtained a percentage of 68.19percent which was greater than the thermal method which was 60.32percent. The content of element C in the kraft lignin extract shows that there are lignin content from the two extraction methods that have been carried out. Other elements such as O, Na, and S are considered as deposits (impurities) which are also extracted. The content of the impurity is present in a smaller amount in the centrifuge method than the thermal method. So it can be concluded that extraction using the centrifuge method is more optimal in separating lignin compared to extraction using the thermal method.

4. Conclusion

The use of black liquor from the side results of cooking in the pulp and paper industry as a source of energy in steam production can be done through purification by extracting lignin compounds using the acid hydrolysis method.

The kraft lignin extraction process uses the acid hydrolysis method with the help of a gradual centrifuge more optimum than the acid and thermal hydrolysis method. Quantitatively calculated with ASL values difference of around 0.002 mg / g both the method and the air value centrifuge give an average yield of 969.815 mg / g, while using thermal assistance gives an average yield of 679.790 mg / g. Qualitatively the comparison of the centrifuge method is more optimal compared to the thermal method indicated by the results of icp, ftir and sem testing.

The results of the kraft lignin extract can be used as an additional chemical in the papermaking process to improve the physical and optical properties of the paper products produced.

5. References

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