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Isolation and characterization of formacell Lignins from oil empty fruits bunches

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Abstract. Lignin is the largest component in black liquor, it is about 46% of solids total and can be isolated by precipitation using acid and base method. The purpose of this study was to get the best NaOH concentration to produce lignin with yield, solids total content, metoxyle lignins content, weights equivalent of lignin in the black liquor by pulping *formacell* process from oil empty fruits bunches. This study was done with isolation lignin process in black liquor used by NaOH concentration were 5%, 10%, 15%, 20%, 25%, and 30% from volume black liquor and then precipitationed for 10 hours. The result of this research showed the isolation of lignin with NaOH concentration 30% get the pH 5,42%, yield of lignin was 5,67%, solids black liquor total was 65,11%, levels of metoxyle lignin 14,61%, and equivalent weights of lignin was 1787,23. The result of FT-IR identifications of isolates lignin in NaOH concentration 25 and 30% showed a pattern infiltration spektro IR that almost a part that have the same infiltration at the wave numbers that showed lignin had one of the rings lignin was guaiasil, it was building blocks of non wood lignin.

1. Introduction

Black liquor is dark liquid from byproduct of the process that transforms wood into pulp, which is then dried to make paper. Black liquor contains lignin, which is the material in trees that binds wood fibers together and makes them rigid, and which must be removed from wood fibers to create paper. Black liquor is a problem in the pulp and paper industry because it is highly polluting the environment [1], and the rejection of this effluent in nature without any treatment is responsible for serious damage to the environment and constitutes a threat for human health. The black liquor consists of almost all the inorganic chemicals used in pulping and organics in the form of dissolved wood constituents [2]. Lignin in the black liquor, is a mixture of polyphenolic compounds with complex chemical structure that resists to conventional biological treatment processes due to their non-biodegradable nature. The presence of dark colored lignin cause s limiting ligh trasmission in aquatic plants. Lignin in black liquor also contains aliphatic acids, acids, resins and polysaccharides increase the burden of oxygen demand in water. Component of black liquor is lignin which is about 46% of its total solid [3], therefore isolation and separation of lignin is more likely. Black liquor can be a source of lignin feedstock[1][4] [5] [6][7][8][9]. Lignin structure and physico chemical properties depends on isolation method and raw material source [10][11]. Black liquor can be isolated alkaline method or acid method to obtain pure lignin. The research trend is an attempt to harness lignin into more useful chemicals [12]. Commercial use of lignin maybe used carbon fiber, adhesive, polyurethane, polyester, bioplastic, and bio oil for petroleum mixtures of fossils [5,9,13,14,15]. The presence of phenolic ring inside lignin can be utilized for phenolic formaldehyde resins [4,5,6,7,16]. Beside lignin can be used as a filler and reinforcing phases for polymer blends [17,18,19,20,21,22]. The advantage of lignin is to have a high number hidroxyl group can be used for the production of polyol and either through direct utilization or after chemical modification for the production of certain polymers such as polyurethane [23,24,25].

In the world it is attempting to utilize black liquor as a source of lignin feedstock. Some lignin isolation methods include: 1). Klason Method; 2). The Björkman method is also called "Milled Wood Lignin / MWL"; 3). CEL Method, Cellulolythic Enzyme Lignin or "lignin of cellulolytic enzymes"; 4). Technical Lignin Isolation Method, namely the lignin isolation method of residual pulp liquor. The process of lignin isolation from black liquor can use acids such as H_2SO_4, phosphoric acid (H_3PO_4), or HCl [26, 27]. While the basic method can use bases such as NaOH and KOH [28]. In this step about 75% of the lignin is precipitated as the sodium salt. Finally, lignin is separated through a screening process Lignin hydrolysis contains solid lignin residues and large amounts of unhydrolyzed cellulose [27].

The characterization of softwoods and hardwoods black liquor from the pulping of non-wood fibers such as reed canary grass, sugarcane baggasse, wheat straw have been investigated lately. However, none works had been done on the black liquor from black liquor formacell EOFB pulping process. Formacell is one of the organosolved pulping methods that use acetic acid and formic acid as cooking solution [29,30,31,32]. The pressure and temperature can be lower when formic acid is used in pulping compared to those used in alcohol or acetic acid pulping. The advantage of organic acid lignin is an optimal feedstock for many value-added products, due to its lower molecular weight and higher reactivity and organic acid pulping is the retention of silica on the pulp fiber that facilitates the efficient recovery of cooking chemicals.

One research reported that only concentrated on lignin isolation from oil palm black liquor and minor on characterization of lignin [22]. Kraft Black liquor from EOFB resulted optimum lignin precipitation was obtained at pH 2 and comparably result could be obtained at pH 4.5 followed by 1 hour heating by addition of anthraquinone (AQ) in the pulping process showed an improved carbohydrates stabilization and better delignification. NaOH extraction was used in order to obtain lignin for use production of polyurethane [34]. The aim of this research is to know the effect of NaOH concentration in isolation process and lignin characterization on the formacell black liquor from empty palm oil bunches. The use of NaOH in the isolation process can be used to precipitate lignin from black liquor.

2. Methodology

2.1. Raw material

The materials used in this research are black liquor from EOFB formacell pulping, NaCl, NaOH, HCl, water, aquades, ethanol, KBr, filter paper, phenolpthalin indicator, aluminum foil, and clip. The tools used in this research are acid cabinet, acid stove, aluminum cup, digital scales, porcelain cup, oven, desiccator, beaker glass, erlenmeyer, pH meter, dropper drop, volume pipette, stirrer, measuring cup, Funnel, centrifuge, stirrer, titration device and FT-IR (Fourier Transform Infra-Red Spectroscopy) spectrophotometer and SEM (Scanning Electron Microscopy)

2.2. Research methods

This research begins with the process of purifying liquid waste from pulp filtration (black liquor) by using lignin isolation method which refers to isolation method developed by Lubis [35] as shown in Figure 1. A total of 100 ml of filtered black liquor (filtrate) Precipitated lignin by stirring and adding by NaOH with concentrations of 5%, 10%, 15%, 20%, 25%, and 30% (percent v / v) of black liquor volume which then homogenized using a stirrer. Stirring process is done slowly then measured pH of each treatment, then subsequently settled for 10 hours for perfect deposition. The lignin deposit is separated from black liquor using centrifuge (2500 rpm, 20 min). The observations were: pH value, total solids content in black leachate EOFB, lignin yield, lignin methoxyl content, lignin equivalent weight, and lignin analysis with FT-IR spectrophotometer and Scanning electron microscopy (SEM) has been most useful technique for quantification of lignin structural details.

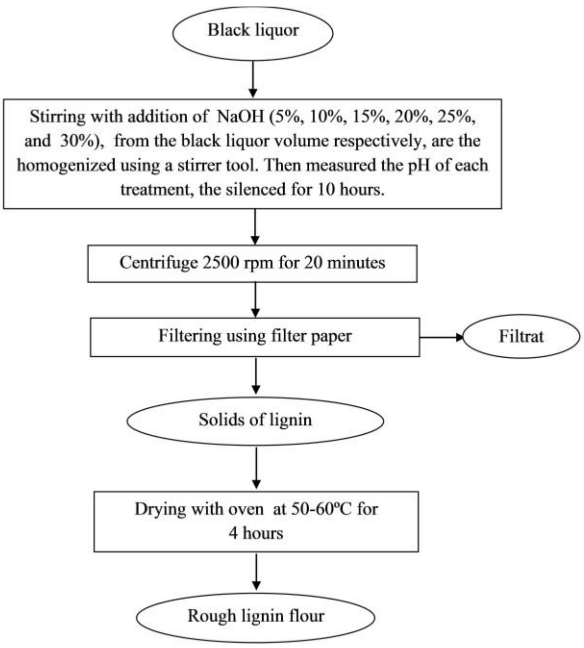


Figure 1. The modified lignin isolation diagram [35]

3. Results and discussion

3.1. Yield of Lignin

The yield was also found to increase for black liquor with a higher total dry solid (TDS) content. The average value of lignin isolate content from various concentrations ranged from 1.48% - 5.67% (Figure 2). The result of variance analysis showed that the NaOH concentration teatment had highly significant effect on yield of lignin.

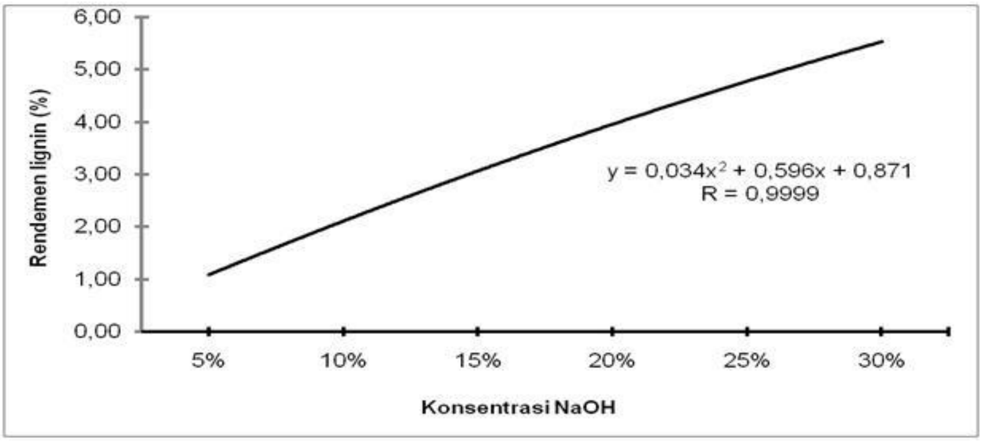


Figure 2. Effect of NaOH concentration on lignin yield

The coagulation of lignin from black liquor occur because the protonation of ionized phenolic group on the lignin molecul. The protonation of phenolic group reduces the electristatic repulsive forces between lignin molecules [36,37] which then become less hydrophylic, leading to precipitation. The highest yield of lignin isolate was found at 30% NaOH concentration with an average of 5.67%. The yield of precipitated activated lignin was influenced by NaOH concentration [38]. The yield of isolate lignin due to the influence of addition factor of NaOH concentration give effect to yield yield of lignin isolate [39]. Yield/equilibrium in the precipitation step of lignoboost process is influenced by diferrent proces condition, i.e, the pH, temperatur and ion strength of black liquor) [41][42]. In this study showed that the yield of lignin isolate tended to increase according to the addition of NaOH concentration as lignin sedimentation solution. The increase of lignin isolate content in the deposition process using NaOH with concentration of 5%, 10%, 15%, 20%, 25%, and 30%, due to the more basic precipitation process where the higher the NaOH concentration the higher the level of base, It is suspected that there is an increasing condensation reaction in the lignin-making units such as para-koumaril alcohol, coniferyl alcohol, and sinapyl alcohol, which will initially undergo repolymerization and form larger molecules of lignin polymer. The higher the concentration, the higher the lignin deposits produced [42]. It is suspected that because of the higher concentration of added NaOH, the OHO ions are consumed by acetyl groups of wood shale during cooking, so the OH^{-} ion not only dissolves lignin but dissolves other non-lignin components [39]. In this study, the highest lignin precipitate was obtained at an average pH of 5.42 with a 30% NaOH concentration. Increasing the concentration of NaOH results in an increase in pH value due to the addition of base or high alkalinity of the substance increases many OH-ions in water. The greater the pH value of a substance the stronger the degree of base The strength of base can be determined from the scale of basicity which is also expressed by pH value [28].

3.2. Lignin Methoxyl Levels

Methoxyl lignin content in this study has an average value ranges between 14.61 - 20.77% (Figure 3). The result of variance analysis showed that the NaOH concentration treatment had very significant effect on lignin methoxyl content.

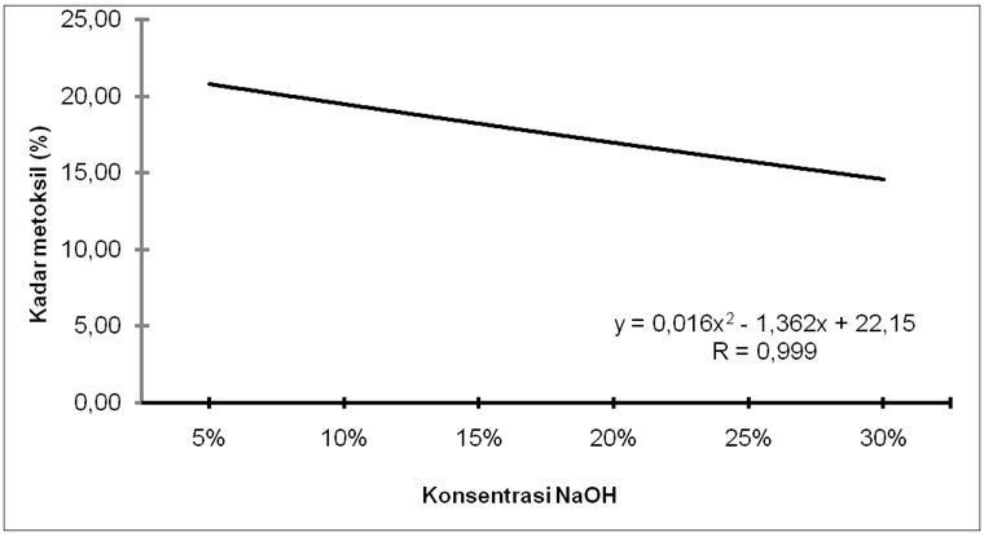


Figure 3. Effect of NaOH concentration on methoxyl lignin levels

The highest levels of methoxyl lignin are present in the addition of 5% NaOH concentration with an average of 20.77%. While the lowest methoxyl lignin levels were found in the addition of 30% NaOH concentration with an average of 14.61%. In general, high methoxyl levels will inhibit lignin reactivity during resin use. Lignin contains phenolic hydroxyl groups which are mostly bonded with adjacent propane phenyl units, allowing the occurrence of lignin bonds with formaldehyde similar to those of a reaction between phenol and formaldehyde [43]. However, in its use as a raw material of lignosulfonate (surfactant), lignin with high methoxyl content is more advantageous because the more -OCH 3 groups contained in lignin, the lignin is increasingly dissolved in water. Such properties are indispensable to lignosulfonate feedstocks.

Meanwhile, low methoxyl levels are suspected because some of the methoxyl groups are degraded and turned into other compounds due to the overuse of acid or base. In alkaline process, phenolic hydroxyl groups are generated by hydrolysis of β-O-4 bond. Low metoxyl levels are caused by changes in methoxyl groups to methyl mercaptan, methyl sulfide, and dimethyl disulfide According

[44]. According to Fengel and Wegener [45], this low metoxyl value is probably caused by the influence of harsh chemicals during isolation, causing the lignin structure to undergo many changes. Low lignin methoxyl levels can be utilized in their use as an adhesive, lignin with a lower methoxyl content is more advantageous than high methoxyl levels, since lignin with low methoxyl content is easier to form gel [46].

3.3. **Lignin's Equivalent Weight**

The average value of the lignin equivalent weight ranges from 1327.64 - 1787.23 (Figure 4). The result of variance analysis showed that the NaOH concentration treatment had very significant effect on the weight of lignin equivalent.

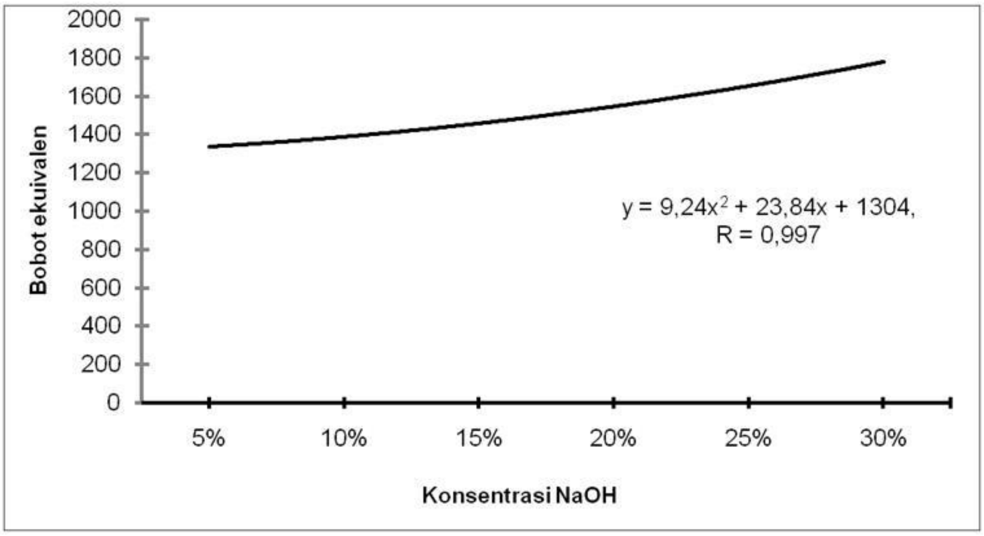


Figure 4. Effect of NaOH concentration on lignin equivalent weight level

At 30% NaOH concentration yields the highest weight of lignin equivalent weight with an average of 1787.23. Meanwhile, the lowest equivalent weight was generated in isolation condition using 5% NaOH concentration with an average of 1327.64. The higher the NaOH concentration as the settling solution, causing the higher lignin equivalent weight. The higher the equivalent weight of a lignin indicates that in lignin insulation, the polymerization proceeds perfectly. In addition, according to Achmadi (1990), the more basic concentrations used at the time of isolation cause lignin to tend to condensate. The condensed lignin composing units form larger molecules so that the weight of the lignin equivalent is increased. The high equivalent weight of EOFB lignin isolates is caused by the lignin structure of EOFB fibers more complex than the lignin structure extracted from the wood. This is due to the complex arrangement of siringil and guaiasil propane units with para-koumaril propane units in EOFB fibers. The standard molecular weight is unknown but is a multiple of 840, the molecular weight of the lignin-making unit [41,47] states the results show that the precipitation yield of lignin increases with decreasing pH and temperature and/or with increasing ion strength of kraft black liquor used. The concentration of carbohydrates in lignin decreases with decreasing pH or with increasing temperature, and that an increasing amount of lower molecular weight lignin is precipitated at a higher precipitation yield. This principle is similar to the lignin isolation process using NaOH . According to Santoso [48], the distribution of molecular weight of lignin varies greatly. Lignin is a very complex organic compound, composed of a number of highly variable constituent components, it is difficult to obtain definite molecular weights. By means of chromatographic separation obtained data of lignin molecule weights range of 370-44300 [49]. b. While the results of research [48] states the molecular weight of lignin isolates from black liquor ranged from 304-4010. Based on the equivalent weight obtained in this study, it meets the criteria based on according to Connors *et al*. [49] and Santoso [48].

3.4. **Lignin Analysis with FT-IR Spectrophotometer**

The following is the result of lignin analysis using FT-IR spectrophotometer, using the best sample that is the addition of 25% NaOH concentration is presented in Figure 5 and the addition of 30% NaOH concentration is presented in Figure 6. FTIR was performed to analyze the differentes in the functional groups of the different lignin samples obtained (Namane *et al*, 2016). The FTIR spectrum of commercial kraft lignin (Indulin AT) was utilized as reference.

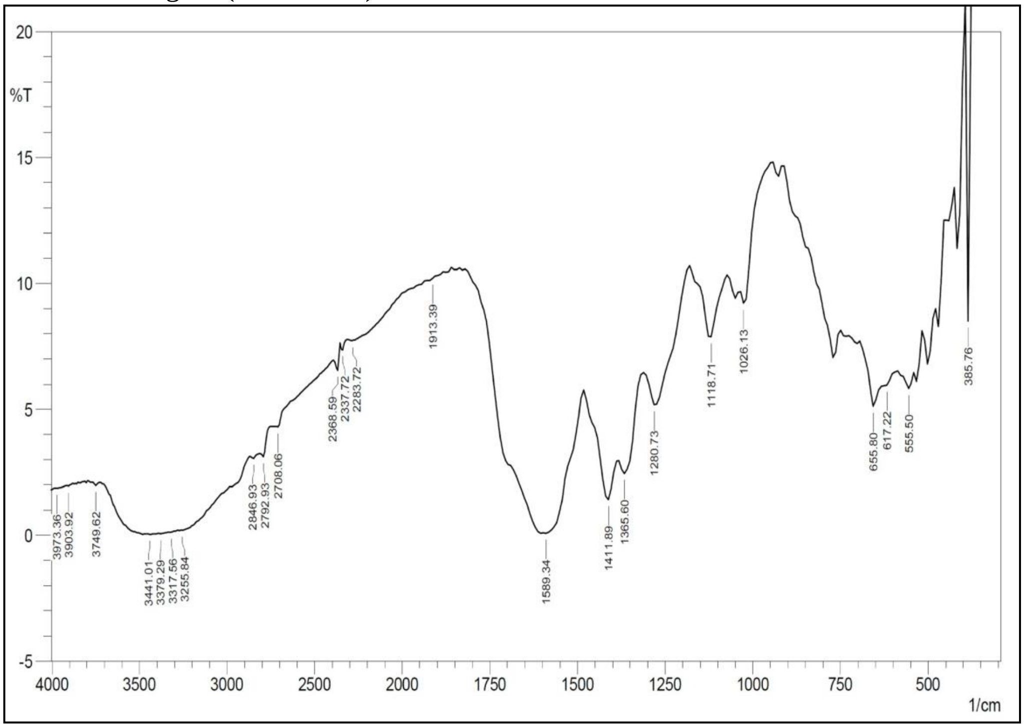


Figure 5. Results of identification with FT-IR spectrophotometer on lignin isolates from EOFB formacell black liquor results in the addition of NaOH concentration of 25%

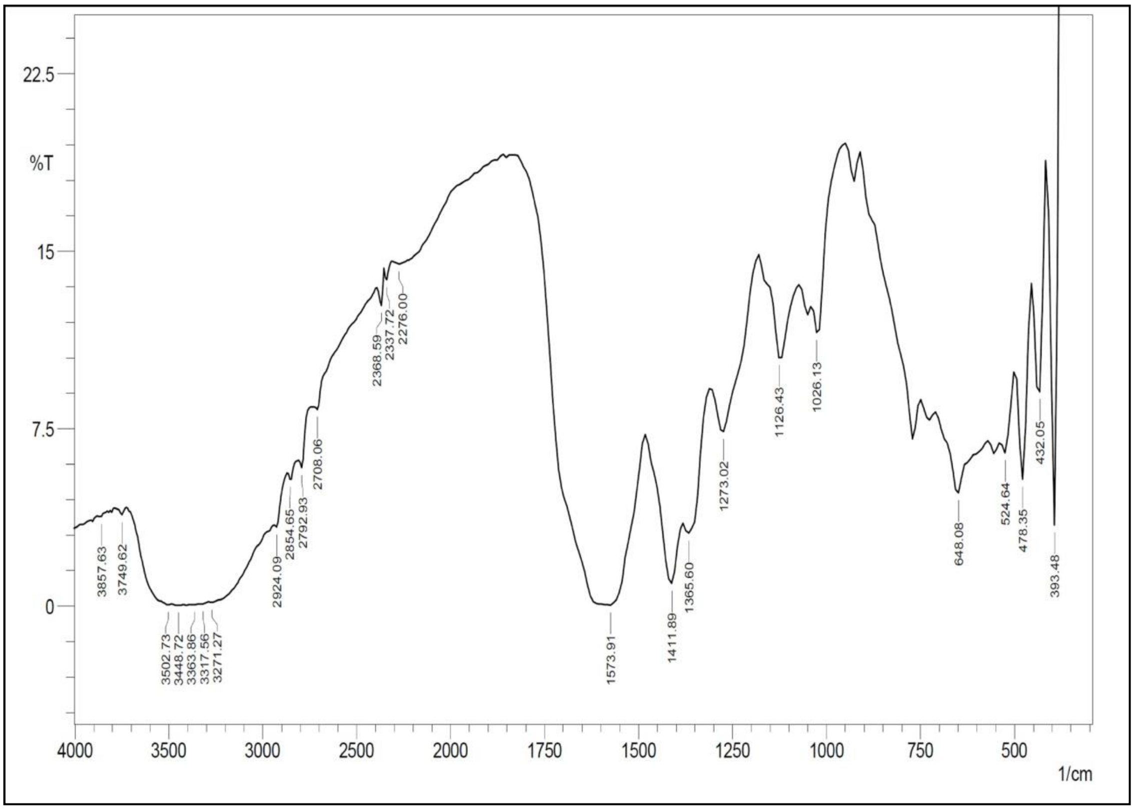


Figure 6. Results of identification with FT-IR spectrophotometer on lignin isolates from EOFB formacell black liquor results in addition of 30% NaOH concentration

Table 1. Fourier transform infrared of two lignin samples [41,50]

No	Lignin isolate NaOH 25%	Lignin isolate NaOH 30%	Indulin-AT	Band Posision (cm-1)*)	Asignment
1	3441.01		3411.36	3450-3400	OH stretch
2	2846.93		2936.36	2940-2820	OH strain on the methyl and methylene groups
3	-		-	1715-1710	The C = O range is unconjugated

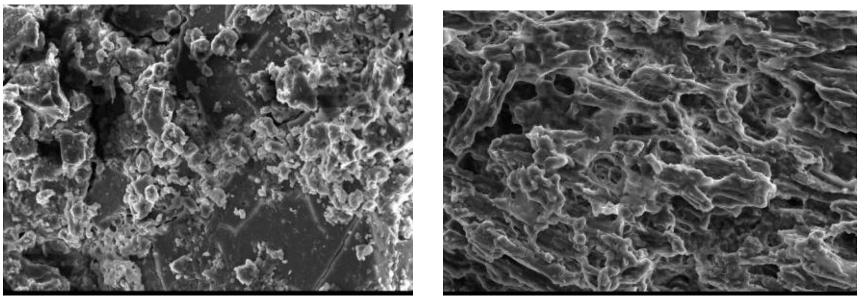
					with an aromatic ring
4	-		1668.18	1675-1660	The C = O range is unconjugated with an aromatic ring
5	-		1602.27	1605-1600	Vibration of aromatic rings
6	1589.35	1573.91		1595	Aromatic sceletal vibration, C=O stetching (conjugated)
7	-		1511.36	1515-1505	Vibration of aromatic rings
8	-		1465.91	1470-1460	C-H deformation (asymmetry
9	-		1427.27	1430-1425	Vibration of aromatic rings
10	1365.60		1365.91	1370-1365	In-plane deformation vibration of phenolic OH
11	-		-	1330-1325	Vibration of siringyl ring
12	1273	1273.03	1270.45	1270-1275	Vibration of guaiacyl rings
13	-		1031.82	1085-1030	Deformation of C-H and C-O
14	1026.13	1026.13		1030	C-O of syringyl and guaiacyl ring, C-H bond in guaiacyl ring

The best isolation conditions were lignin isolates with 25% and 30% NaOH concentrations. The lignin isolates were compared with the standard lignin used ie lignin indulin-AT. The purpose of the functional group analysis is to know the functional groups present in lignin from the isolated and standard lignin products used. The two bands at 2900 cm-1 and 2800 cm-1 correspond to methyl (−CH3) and methylene (−CH2) groups. The phenolic OH groups in lignin (band at 1365 cm-1), are produced during chemical process when β-O-4 linkages are cleaved and generate non-etherified hydroxyls. Low intensity of this band in NaOH 30% spectrum shows that small portion of phenolic OH group is generated (due to less β-O-4 linkage cleavage). The intensity of absorption bands at 1268 cm-1 (C-O stretching of guaiacyl ring) spectra is stronger than other lignins because guaiacyl is dominant lignin unit in EOFB. The absorption band range 1030-1025 cm-1 is assigned to deformation vibration of C−H bonds in the guaiacyl ring and also assigned to C-O bonds in both syringyl and guaiacyl [41]. Bands at 1330-1325 cm-1 were attributed to syringil with C-O stretching. Bands at 1217 cm-1 for OPEFB can be attribute to phenolic OH and ether in syringil and guaiacyl [52]. The bands observed at 1030-620 cm-1 were attributed to hemicelluloses and silicates contribution [51].

Lignin is a complex polymer synthesized mainly from three hydroxycinnamyl alcohols differing in their degree of methoxylation: *p*-coumaryl, coniferyl, and sinapyl alcohols [53,54,55]. Each of these monolignols gives rise to a different type of lignin unit called *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively, when incorporated into the polymer. Lignin is a polymer of phenolic hydroxyl groups, hydroxyl benzylic and carbonyl groups. The lignin polymer contains characteristic methoxyl groups, hydroxyl phenol groups, and some end-aldehyde groups in the side chain [3]. The presence of absorption bands at wave numbers with a strong intensity of about 1.270-1330 cm-1 in lignin isolates resulting from black liquor of this organosolve delignification process with a 30% NaOH concentration suggests the presence of one of the lignin ligands, ie guaiasil which are the units Lignin constituents in non-wood lignin.

3.5. **Assessment of the structure of OPFEB formacell lignin**

The Scaniing Electrom Miscoscope (SEM) studies revealed the details on structural and marfologies of lignin. Lignin was analyzed by using SEM that is lignin with treatment of NaOH concentration that is 5% and 30% (Figure 7).



(a) (b)

Figure 7. SEM migrographs of lignin samples (a) isolation by 5% NaOH, (b) isolation by 30% NaOH

The result of SEM analysis showed that lignin isolation treatment using 30% NaOH concentration had a more compact form of agglomeration compared with isolation using 5% NaOH. At the high pH of typical kraft black liquof, the repulsive forces between the ionized hydrophilic groups (mainly phenolic hydroxyl and carboxylate groups) stabilize the colloidal lignin and keep it in solution, thereby preventing lignin agglomeration and precipitation [56]. The results of Namane *et al* [57] showed that the lignin isolation process from liquor derived from formacell produces a constant granular structure.

4. **Conclusion**

The best lignin isolates were on lignin deposition with 30% NaOH concentration by total solids content in EOFB black liquor, lignin of yield, lignin methoxyl content, lignin equivalent weight, The average lignin yield is 5.67%, the total solid black liquor with an average of 65.11%, the lignin methoxyl content with an average of 14.61% and the weight of the lignin equivalent with an average of 1787.23.. The result of FT-IR identification from lignin isolate at 30% NaOH concentration shows IR spectral absorption pattern which almost most have the same absorption pattern at wave number region. Isolates of lignin at a 30% NaOH concentration showed that lignin has one lignin ring ie guaiasil which is lignin composing units in non-wood lignin.

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