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The Oxidation of Cellulose from Oil Palm Empty Fruit Bunch by using Hydrogen Peroxide in Alkaline Condition

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Oksidasi Selulosa dari Tandan Kosong Kelapa Sawit menggunakan Hidrogen Peroksida dalam Kondisi Basa

Abstrak

Perhatian untuk memanfaatkan selulosa sebagai polimer terbarukan untuk menggantikan polimer tidak terbarukan mengalami peningkatan. Perubahan dan modifikasi kimia selulosa melalui proses oksidasi diperlukan untuk meningkatkan sifat dan fungsi selulosa. Penelitian ini bertujuan untuk mempelajari pengaruh oksidasi selulosa dari tandan kosong kelapa sawit (TKKS) menggunakan hidrogen peroksida dalam suasana basa. Selulosa diisolasi dan dimurnikan dengan metode natrium hidroksida dan dilanjutkan dengan pemutihan natrium hipoklorit. Efek oksidasi selulosa oleh hidrogen peroksida dievaluasi menggunakan analisis komponen lignoselulosa, analisis visual, sifat fisik dan kimia. Analisis spektroskopi inframerah (FTIR) digunakan untuk mengevaluasi perubahan gugus fungsional selulosa. Pemasakan TKKS dengan natrium hidroksida pada suhu160^{o}C selama 4 jam mengurangi kandungan lignin dari 22,58% menjadi 16,60%, meningkatkan kandungan selulosa dari 60,76% menjadi 73,87% dan hemiselulosa dari 25,86% menjadi 30,95%. Perlakuan pulp TKKS menggunakan natrium hipoklorit menghilangkan semua sisa lignin. Kandungan selulosa meningkat hingga 90,86%. Oksidasi selulosa dengan hidrogen peroksida menurunkan derajat polimerisasi selulosa dari 1997 menjadi 658. Gugus karboksil selulosa meningkat secara signifikan dan dikonfirmasi dengan analisis titrasi. Analisis visual menunjukkan kerusakan serabut selulosa, sesuai dengan pengurangan kristalinitas selulosa.

Kata kunci: selulosa, oksidasi, tandan kosong kelapa sawit, gugus karboksil, kristalinitas, sifat fisik

Abstract

There are growing interest to use cellulose as renewable material in order to replace non-renewable polymeric materials. Alteration and chemical modifications of the cellulose by oxidation is needed to improve its properties and functionality. The aim of this study was to evaluate oxidation effect of the cellulose from oil palm empty fruit bunch (OPEFB) using hydrogen peroxide in alkaline condition. Cellulose has been isolated and purified by sodium hydroxide method followed by sodium hypochlorite bleaching. The oxidation effect of the cellulose by hydrogen peroxide was investigated by component analysis of the lignocelluloses, visual analysis, physical and chemical properties. Fourier transform infrared spectroscopy was employed to evaluate the changes of functional groups. Digesting of the OPEFB by sodium hydroxide at temperature 160^{o}C for 4 hours reduced lignin content from 22.58% to 16.60%, increase cellulose and hemicelluloses content from 60.76% to 73.87% and 25.86% to 30.95%, respectively. Treatment of the OPEFB pulp using sodium hypochlorite removed all residual lignin. Cellulose content was increased up to 90.86%. Degree of polymerization of the oxidized cellulose was reduced from 1997 to 658. Carboxyl groups of celluloses was significantly increased and confirmed by titration analysis. OPEFB cellulose fiber was damage and broken, meanwhile crystallinity of the cellulose was reduced.

Keywords: cellulose, oxidation, oil palm empty fruit bunch, carboxyl group, crystallinity, physical properties

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Introduction

There are growing interest to replace non-renewable polymeric materials obtained from petrochemical resource by renewable polymers such as cellulose. Cellulose has been used for long time as fiber source in paper industry. Recently, cellulose also uses for many application, i.e.: biofuel (Piarpuzán *et al*., 2011), bioplastic (Shen *et al*., 2010), and composite (Varshney & Naithani, 2011). Biomass waste from agro-industry is a good source for high cellulose content, such as oil palm empty fruit bunch (OPEFB). Indonesia is the largest oil palm producers in the world, where its production is predicted as about 31 million metric tons of oil palm in 2015 (Dirjenbun, 2015). Crude oil palm (CPO) is extracted from the fruits and the lignocelluloses residual remains as OPEFB. Accumulation of OPEFB in the mill reaches about 28.65 million metric tons per year. OPEFB has low commercial value and constitutes a disposal problem due to its large quantity. Therefore, it is of importance to optimally utilize OPEFB in order to solve these problems and at the same time transform the resources for valuable products.

OPEFB is composed of 40.37% cellulose, 20.06% hemicelluloses, and 23.89% lignin (Isroi, 2015). Having high cellulose content, OPEFB has high potential to be used as a source for cellulose and cellulosic derived products. Various researches and developments have been conducted to produce cellulose and cellulosic derived product from OPEFB, such as cellulose fiber (Khalid *et al*., 2008), nano-cellulose (Lani *et al*., 2014; Zianor Azrina *et al*., 2017; Mohd *et al*., 2017), glucose (Hamzah *et al*., 2011), xylose (Zhang *et al*., 2012), ethanol (Isroi *et al*., 2014; Sklavounos *et al*., 2013), and citric acid (Bari *et al*., 2010). However, the production of cellulose and cellulose derivate is often cumbersome process because cellulose is naturally immersed with other matrix (lignin and hemicelluloses) and it has low reactivity due to large amount of hydrogen bonds which restrict its solubility in all common solvents (Swatloski *et al*., 2002).

Alteration and chemical modifications of the cellulose are applied during processing and producing of cellulose material. Cellulose modification through oxidation leads to added value products in order to determine macroscopic properties and chemical behavior of cellulosic materials. Cellulose is oxidized when the functional group of carboxylic acids is replaced by one or more of the hydroxyl groups positioned at C2, C3 or C6. The oxidized cellulose containing carboxyl groups grows special interest due to its usefulness in broad applications, such as: medical, agricultural, cosmetic, and pharmaceutical application (Coseri *et al*., 2013). Carbonyl and carboxyl groups in oxidized cellulose play a decisive role in the pulping process and therefore in the final paper properties (Kitaoka *et al*., 1999). Oxidized cellulose fibers have been shown to perform higher sheet density and improved strength-related properties but only if the total carboxyl group content is less than 500 mmol/kg (Ma *et al*., 2010). Cellulose can be oxidized by various oxidizing reagents that can be divided into non-selective (such as: permanganates, peroxides and ozone) and selective (such as: periodates and nitroxyl radicals) (Coseri *et al*., 2013). Hydrogen peroxides has been used in industrial application for pulp bleaching (Brooks & Moore, 2000). However, it could equally be used to alter the properties of the cellulose. The aims of this study was to evaluate oxidation effect to cellulose that purified from OPEFB using hydrogen peroxide in alkaline condition.

Materials and Methods

Oil Palm Empty Fruit Bunch

OPEFB was collected from an oil palm mill in Simalungun, North Sumatera, Indonesia. OPEFB used in this study was fresh OPEFB from the mill, chopped directly, and dried in the same day, until the moisture content was less than 10%. Reducing the water content of OPEFB would reduce the decomposition of OPEFB by native microorganism. Chopping and drying processes were also used to remove kernel and other contaminants. Dried EFB was chopped into approximately 5 cm long small pieces and stored in a container at room temperature prior to the experiment. It was analyzed for its lignin, cellulose, and hemicelluloses contents.

Cellulose Preparation

Dried OPEFB was delignified by sodium hydroxide using laboratory rotary digester in the dosage of 10 g NaOH/100g OPEFB with consistency of 10%. Two thousands grams (o.d. basis) of dried OPEFB was put into the

digester and heated to reach pressure at 2 bars and maintained for 4 hours. Pulp was then washed with water to remove NaOH residue and black liquor. The pulp was beaten in laboratory beater to get pulp with freeness level of 300 mL CSF. Sodium hypochlorite (5.25% in water) was used for cellulose purification. A hundred grams of pulp (o.d. basis) was treated in a flask containing 3000 mL of distilled water with 33.5 g sodium hypochlorite at the temperature of 70-75^{o}C. The addition of sodium hypochlorite was continued at 2 hours intervals until the cellulose become white. The cellulose was left in acidified condition for 12 hours before washing. Cellulose was washed at least three times to remove all residual sodium hypochlorite.

Oxidation of the Cellulose

Five g OPEFB cellulose (o.d. basis) was added into 1000 mL Erlenmeyer flask. The cellulose was then impregnated by 500 mL of hydrogen peroxide solution with various concentrations (0%, 3%, 6%, and 9%). The pH of the solution was maintained at 11 using 0.1 M NaOH or 0.1 M HCl solution. The cellulose suspension was continuously shaken with electric shaker for 24 hours. In the end of the reaction, pulp was filtered and washed for at least four times. It was then dried prior to subsequent treatment and analysis.

Analytical Methods

The cellulose, hemicelluloses, and lignin of the OPEFB were determined according to the Chesson-Datta Method (Chesson 1981) and TAPPI Standard. A fourier transform infrared (FTIR) spectrometer (Impact 410 iS10, Nicolet Instrument Corp.) was used for determining changes in the structure of the OPEFB, pulp, and cellulose to the method described in reference (Isroi *et al*., 2014). Each spectrum was obtained with an average of 32 scans and resolution of 4 cm^{-1} from 600–4,000 cm^{-1}. The spectrum data was controlled by Nicolet OMNIC 4.1 (Nicolet Instrument Corp.) software and analyzed by eFTIR® (EssentialFTIR, Operant LLC). Fiber and cellulose micro morphology was visualized using light microscope with 400x – 1000x magnification. Crystallinity of the cellulose presented as lateral order index (LOI) according to methods described in the references (Åkerholm *et al*., 2004; Abdul, J. M. Jahim, *et al*., 2016). Degree of polymerization of cellulose was measured by viscometric technique (Hubbell & Ragauskas, 2010).

The carboxyl content of all cellulose samples was determined by a titration technique described elsewhere (Fras & Stana-Kleinschek, 2002). An air-dry cellulose sample equivalent to 0.5-1.0 g was weighted into a 200 mL glass- stopper flask. A hundred mililiters of calcium acetate solution were added. The flasks were shaken overnight, and the suspension of fibers was then filtrated. The color indicator murexide was used as a metal chromic indicator. The pH value of the filtrate was adjusted up to 12 by the addition of 0.1 M sodium hydroxide solution. The decrease in concentration of calcium acetate solution after contact with the fibers was determined by titration technique. Solution of 0.1 M EDTA was used as titrant.

Results and Discussion

Lignocelluloses Content

Initial lignocelluloses component of dried OPEFB is shown in **Table 1**. OPEFB used in this study has high cellulose content and low lignin content compared to other references (Isroi, 2015; Law *et al*., 2007; Rahman *et al*., 2007; Pujiasih *et al*., 2018). Range of the lignocelluloses components of OPEFB were 42.7-65% cellulose, 17.1-33.5% hemicelluloses, and 13.2-25.31% lignin (Shinoj *et al*., 2011). Variation lignocelluloses content of OPEFB could be caused by different raw material source, plant varieties, historic treatment of the OPEFB prior laboratory analysis, and analytical method. OPEFB has highest composition of cellulose compared to other source, such as coir (Haque *et al*., 2009), rice straw (de Assis Castro *et al*., 2017), baggase (Chadijah *et al*., 2018), and kenaf fiber (Alavudeen *et al*., 2015). Having high cellulose content made OPEFB is a potential resource for cellulose and cellulose derivative product.

Table 1. Initial Lignocelluloses Content of Oil Palm Empty Fruit Bunch

Component	(%)
Cellulose	60.76
Hemicelluloses	25.86
Lignin	22.58

Changes of the lignocelluloses content of the OPEFB, pulp and bleached pulp is shown in **Figure 1**. Initial content of the OPEFB was 60.76% cellulose, 25.86% hemicelluloses, and 22.58% lignin. Pulping process of the OPEFB reduce the lignocellulosic content become 73.87% cellulose, 30.95% hemicelluloses, and 16.6% lignin. Lignin content reduced significantly by pulping process and the other components were increased. Lignin is soluble in alkaline solution (i.e. sodium hydroxide), high temperature, and high pressure. On the other hand, cellulose and hemicelluloses are more stable in alkaline solution. Sodium hydroxide was also reported as better chemical to solubilize oil palm fiber than other chemical (Sreekala *et al*. 1997). Alkaline pulping is currently the most widely used method to reduce lignin content in pulp and paper production (Suhas *et al*., 2007).

Bleaching of OPEFB pulp by sodium hypochlorite changed the lignocellulosic content. Cellulose was increased from 73.87% to 90.86%. Hemicelluloses and lignin were reduced from 30.95% to 27.12% and 16.6% to 0%, respectively. Increasing of the cellulose was caused by reducing of the other component. Sodium hypochlorite is strong oxidizing agent and commercially used for pulp and textile bleaching (Taylor *et al*., 1940). In this study, lignin content was totally removed and hemicelluloses were slightly reduced after sodium hypochlorite treatment. In lignocelluloses model, cellulose is covered by hemicelluloses in lignin (Mosier *et al*., 2005). Sodium hypochlorite probably attacked the lignin and hemicelluloses prior to cellulose.

Degree of polymerization (DP) of the cellulose was also changed after pulping and bleaching process as shown in **Figure 2**. Pulping process was slightly reduced DP from 2358 (OPEFB) to 1997 (OPEFB pulp). The DP was significantly reduced after the OPEFB pulp treated by sodium hypochlorite to 658. Sodium hypochlorite seems to cut the cellulose polymer into shorter polymer. The DP of the OPEFB pulp was slightly higher than cellulose fiber from OPEFB reported in the reference (Fahma *et al*., 2010). Cellulose has two regions that are crystalline and amorphous region. Amorphous region is easier to break and hydrolyzed by chemical or physical processes than the crystalline region.

Pulping and bleaching process of the OPEFB was also reduced length of the OPEFB cellulose fiber. Fiber length distribution of the OPEFB, pulp and bleached pulp was shown in **Figure 3**. Native OPEFB pulp was dominated by fiber with 0.5-1.0 mm in length. This native OPEFB fiber length is similar to the reference (Khalil *et al.*, 2008). After pulping process, percentage of the 0.5-1.0 mm fiber length was reduced and percentage of the 0.2-0.5 mm fiber length was increased. Fine fiber (0.2-0.5 mm) dominated after pulp bleaching using sodium hypochlorite. It can be seen that these pulping and bleaching process separated the fiber bundles into smaller and shorter fiber size. This phenomenon is also reported in the reference for kenaf fiber (Jonoobi *et al*., 2009). Treatment of OPEFB could reduce size and dimension of the OPEFB fiber (Norul Izani *et al*., 2013).

Changes of Functional Groups

Changes the functional group of the OPEFB bleached pulp after oxidizing were studied by FTIR analysis. Peak assignment of the FTIR spectra

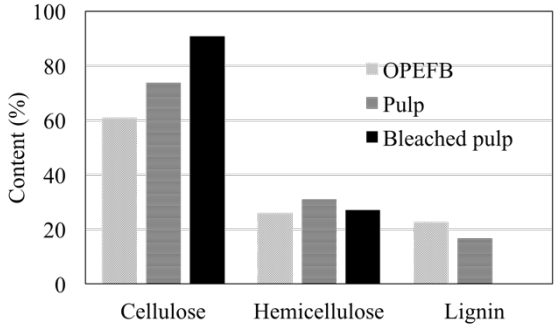

Figure 1. Lignocellulose Component (Cellulose, Hemicellulose and Lignin) of the OPEFB, Pulp, and Bleached Pulp

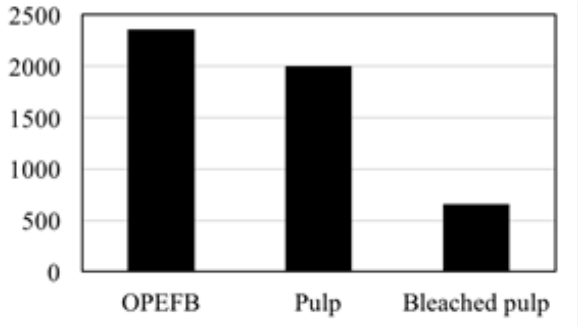

Figure 2. Degree of Polymerization of Oil Palm Empty Fruit Bunch (OPEFB), Pulp, and Bleached Pulp from OPEFB

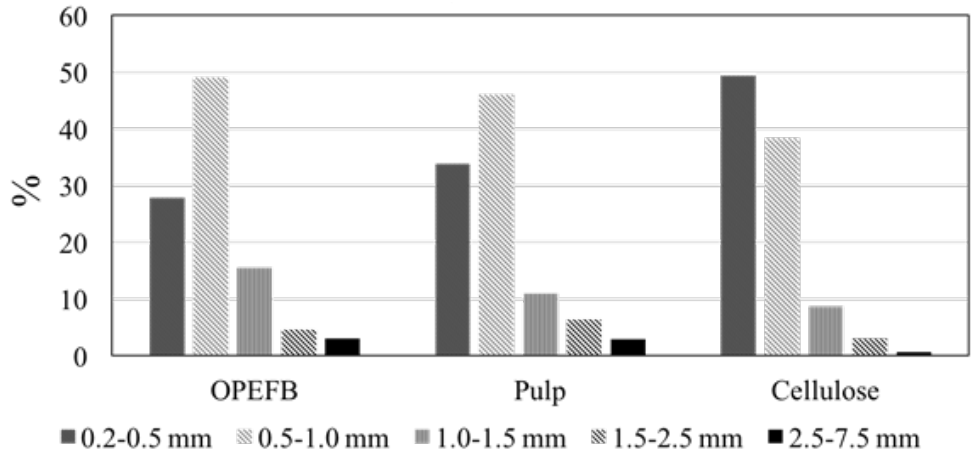

Figure 3. Fiber Length Distribution of Oil Palm Empty Fruit Bunch (OPEFB), Pulp, and Cellulose from OPEFB

was reported in Isroi *et al*., (2014). Hydrogen peroxide is also known as mild oxidizing agent. Hydrogen peroxide can randomly oxidize the cellulose in various sites. Since hydrogen peroxide behaves as a non-selective oxidation agent, the course of oxidation could be altered and different oxidation products could be obtained (Kramar *et al*., 2014). In this study, we found that two peaks of the FTIR spectra were affected by hydrogen peroxide treatment, i.e.: 1722 and 1629 cm^{-1} (**Figure 4**). These peaks are assigned as non-conjugated carboxyl bond and carbonyl bond, respectively (Łojewska *et al*., 2005). In **Figure 4** shown that peak at 1722 and 1639 cm^{-1} were increased by increasing hydrogen hydroxide concentration from 3% to 9%. In control (pulp without sodium hydroxide treatment) 1722 cm^{-1} peak was low. This peak gradually increases with increasing the sodium hydroxide concentration. Increasing of the 1722 cm^{-1} peak was higher than 1629 cm^{-1} peak. There are no significant changes in the peaks 2900-3000 cm^{-1} region. This peaks are assigned to hydrogen bonded (O-H) stretching absorption (Schwanninger *et al*., 2004).

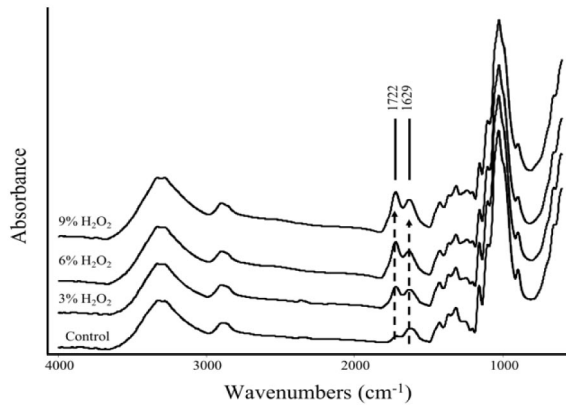

Figure 4. FTIR Absorbance Spectra of Oxidized Cellulose with Different H_2O_2 Concentration

The C atoms in glycopyranose anomer inside the cellulose chain which are the most susceptible to oxidation occupy the 2, 3, and 6 position (Łojewska *et al*., 2005). Oxidation by hydrogen peroxide of the cellulose could be occurring in these C atoms position. C=O stretch at wave number 1722 cm^{-1} could be carboxyl or aldehyde absorptions (Stenstad *et al*., 2008; Łojewska *et al*., 2005). This peak in control (un-oxidized cellulose) could be from residual hemicelluloses (Faix *et al*., 1991), since bleached pulp of OPEFB still have about 27% of hemicelluloses. The carboxyl vibration around 1722 cm^{-1} representing the final oxidation stage of carbon atoms in glycopyranose rings, increase with the increasing of the hydrogen peroxidase concentration (Łojewska *et al*., 2005). Oxidation of cellulose with sodium periodate and sodium chlorite introduces carboxyl groups mainly in position 2 and 3 (Luiz Barbosa). Increasing of the carboxyl group of the bleached pulp after hydrogen peroxidase oxidation which is confirmed by titration analysis is presented in **Figure 5**.

There are several methods to predict the cellulose crystallinity. Crystalinity of the cellulose could be predicted from FTIR peak analysis (Åkerholm *et al*., 2004; Park *et al*., 2010). In our experience, LOI (lateral order index)

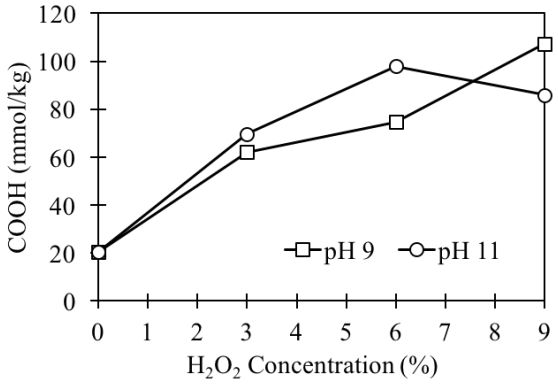

Figure 5. Carboxyl Content of Oxidized Cellulose

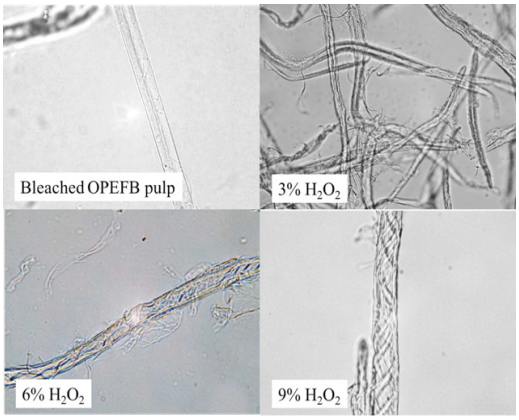

Figure 7. Morphology of The Cellulose Strand Under Light Microscope (400x Magnifications)

is better method for the OPEFB. LOI is ratio between absorbance at wave number 1418 and 895 cm^{-1} (Hurtubise & Krässig, 1960; Spiridon *et al*., 2011). A LOI value of the oxidized cellulose is presented in **Figure 6**. Crystallinity index of the cellulose was decreased by increasing the hydrogen peroxide concentration. LOI value decreased from 0.553 at control (0% H_2O_2) to 0.507 at 9% H_2O_2. Oxidation of the cellulose seemed to disturb and destroy hydrogen bond between cellulose polymers in the crystalline region of the cellulose micro fibril. LOI value of the oxidized cellulose was lower than the OPEFB reported in Abdul, J. Jahim, *et al*., (2016).

Cellulose Morphology

Visual characteristic of the cellulose fiber isolated from OPEFB analyzed using light microscope is shown in **Figure 7**. Cellulose macro fiber of the bleached OPEFB pulp was apparently smooth and bright under the microscope. Oxidation of the cellulose macro fiber resulted hairy fiber. Microfiber of the cellulose is coming out from the macro fiber look like hairy fiber. Increasing the hydrogen peroxide concentration would increase the microfiber. Hemicelluloses that cover and bend the microfiber cellulose could be oxidized by hydrogen peroxide. Degradation of the hemicelluloses would open the cover of cellulose macro fiber and released the cellulose microfiber. Cellulose polymers also bend by hydrogen bond between cellulose strands. Oxidizing the C atom into carbonyl could break the hydrogen bond between cellulose as represent in the decreasing of the cellulose crystallinity. Moreover, oxidized cellulose fiber was thinner than the un-oxidized cellulose.

SEM micrograph study of the OPEFB fiber revealed that the macro fiber was composed of smaller microfiber (Norul Izani *et al*., 2013). Oxidation of the OPEFB cellulose in alkaline condition in this study apparently partially separated the micro fibril cellulose from the fiber bundle. Some fiber linkages were broken up after the treatment. This result confirmed other studies (Zuluaga *et al*., 2009; Sreekala *et al*., 1997). OPEFB micro fibril arranged in spiral in the fibril as is shown in **Figure 6** at 9% H_2O_2. This evidence supported proposed model of the cellulose in vascular bundle of the OPEFB (Khalil *et al*., 2012).

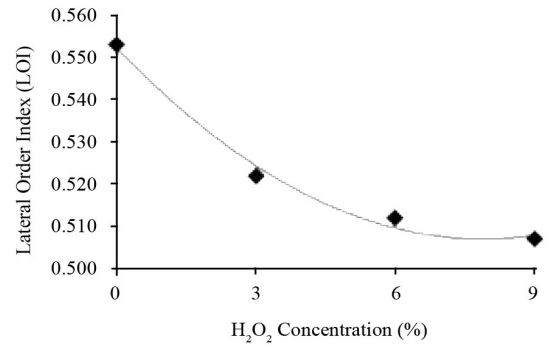

Figure 6. Lateral Order Index (LOI) of The EFB Cellulose Oxidized in Different H_2O_2 Concentration: 0% (Control), 3%, 6% and 9%

Conclusions

Cellulose was successfully isolated from OPEFB by sodium hydroxide method following

by sodium hypochlorite treatment. Treatment of the OPEFB by 10% sodium hydroxide at 2 bars for 6 hours was the best condition to reduce lignin content. Cellulose, hemicelluloses and lignin content of the pulp changed from 60.76% to 73.87%, 25.86% to 30.95%, and 22.58% to 16.60%, respectively. Bleaching of the pulp using sodium hypochlorite (5.25% in water) increase cellulose content to 90.86% and totally reduced lignin content to 0%. Carbonyl content of the bleached pulp increased by increasing the hydrogen peroxide concentration. Carboxyl content at 9% hydrogen peroxide was 107.26 mmol/kg (pH 9) and 85.86 mmol/kg (pH 11). Oxidation of the bleached pulp was also affected the macro fibril resulted hairy microfiber coming out from the cellulose macro fiber. The oxidized cellulose could has better compatibility with others polymers to make a composite materials.

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