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# MONITORING QUALITY OF SODA BLACK LIQUOR OF OIL PALM EMPTY FRUIT BUNCH FIBERS IN TERMS OF STORAGE TIME AND TEMPERATURE

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**Abstract:** The quality of black liquor from oil palm empty fruit bunch fibers pulping was determined through direct isolation of soda lignin using 10% hydrochloric acid at three pH fractions, i.e. pH 2, pH 4 and pH 6. Destructive methods such as nitrobenzene oxidation and ash contents determination were used in the study. pH 2 was found to be the most preferable fraction due to the highest lignin yield. Nitrobenzene oxidation showed that the predominant compound was vanillin, which was in the range of 44.9-52.1% of the total product. Syringaldehyde was the second major compound (ca. 21.5-30.8%), followed by *p*-hydroxybenzaldehyde. The moisture and the ash contents of pH 6 fraction were the highest followed by pH 4 fraction and pH 2 fraction, especially at longer storage time. Soda lignin has to be isolated in less than 15 days of storage regardless of storage temperature to prevent high rate of biodegradation activities.

*Keywords*: Black liquor, lignin, oil palm empty fruit bunch fibers, storage time, storage temperature

**Abstrak:** Kualiti likuor hitam daripada proses pemulpaan tandan buah sawit kosong ditentukan melalui kaedah pemencilan langsung lignin soda dengan asid hidroklorik 10% pada tiga nilai pH iaitu 2, 4 dan 6. Kaedah memusnah seperti pengokisidaan nitrobenzena dan penentuan kandungan abu digunakan dalam kajian ini. pH 2 didapati memberi dapatan lignin yang tertinggi. Melalui ujian pengoksidaan nitrobenzena, vanilin adalah sebatian utama yang mewakili 44.9-52.1% daripada jumlah produk. Siringaldehid pula merupakan sebatian kedua utama yang mewakili 23.1-30.8%, dan seterusnya diikuti pula oleh *p*-hidroksibenzaldehid. Kelembapan dan kandungan abu bagi sampel lignin yang dipencilkan pada pH 6 adalah yang tertinggi diikuti oleh pH 4 dan pH 2 terutamanya apabila disimpan lama. Kajian ini mendapati, bagi kedua-dua suhu penyimpanan, lignin soda perlu dipencilkan sebelum mencapai tempoh penyimpanan selama 15 hari untuk mengelakkan kadar aktiviti biodegredasi yang tinggi.

*Kata kunci*: Likuor hitam, lignin, serat tandan buah sawit kosong, masa penyimpanan, suhu penyimpanan

## 1.0 INTRODUCTION

Malaysia has over 2.5 million hectares of oil palm plantations that could yield more than 8 million tones of empty fruit bunches (EFB) annually. The enormous amount of EFB generated from palm oil milling operations pose serious environmental threat to the society. Fibrous derivatives from empty fruit bunch represent a renewable source

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of non-wood lignocellulosic materials, which has created considerable research interests, especially in the pulping and composite industry [1-5].

In pulp and paper mill, large volume of the spent liquor from the pulped could be recycled in order to recover lignin rather than discarded into waste. Precipitation of lignin from the black liquor was reported by a number of researchers using mineral acids [6-12].

Lignin is a polyphenolic compound arising from an enzyme-mediated dehydrogenates polymerization of three major phenylpropanoid monomers, syringyl alcohol, guaiacyl alcohol and *p*-coumaric alcohol [13]. Lignin is linked by carbon-carbon and ether bonds to form tri-dimensional network associated with the hemicelluloses polysaccharides inside the cell wall [12]. Due to the cross-linking, lignin is generally insoluble in all solvent and only degrade by physical or chemical treatments [14]. During the chemical pulping process at high-temperature and high-pressure under aqueous alkaline, acidic or neutral, lignin tends to degrade from hemicelluloses and dissolve into the spent liquor. The delignification reactions involved the cleavage of non-phenolic $\beta$-O-4 linkage, phenolic $\alpha$-O-4 linkage and releasing from the associated by the polysaccharide [15-16].

The objective of this study is to gain a better understanding on the quality of the black liquor from EFB pulping against the storage time and storage temperature, corresponding to the soda lignin isolated from the black liquor by 10% of hydrochloric acid at three pH fractions (pH 2, pH 4 and pH 6). The obtained lignin was further characterized using destructive techniques, which were nitrobenzene oxidation and ash content.

## 2.0 EXPERIMENTAL

### 2.1 Material

The raw material used in this study was oil palm empty fruit bunch (EFB) fiber supplied by Sabutek (M) Sdn. Bhd., a Malaysian company specializing in recycling of EFB fiber.

### 2.2 Pulping Conditions

The EFB fiber was pulped in a 20 L stainless steel rotary digester unit with 25% NaOH (cooking liquor) for 3 hours at a maximum cooking temperature of 170°C. The cooking liquor to the EFB fiber ratio was 10:1. Prior to the pulping process, the fiber was soaked in water for 2 days, cleaned and dried.

### 2.3 Storage Conditions

The black liquor collected from the pulping process was stored in plastics bottles. Five of the bottles were stored in the refrigerator and the rest were stored at room temperature. After the 5th day of storage, two bottles (one from the refrigerator and one from room temperature) were taken for lignin isolation. This step was repeated after the 15th, 30th, 60th and 90th day of storage.

## 2.4 Lignin Isolation

The pH and density of black liquor obtained from the pulping process was 12.45 and 1.02 g/mL respectively. The soda lignin was precipitated from the concentrated black liquor by acidifying it to pH 2, pH 4 or pH 6 using 10% v/v of hydrochloric acid. The precipitated lignin was filtered and washed with pH water corresponding to its pH fraction. The soda lignin was then dried in a vacuum oven at 55°C for 24 hours prior for further analysis.

## 2.5 Lignin Analysis

Nitrobenzene oxidation was carried out by adding 50 mg dry lignin into a mixture of 7 mL of 2 M NaOH and 4 mL of nitrobenzene in a 15 mL steel autoclave. The autoclave sealed was tightened with a screw cap fitted with Teflon gasket and heated at 165°C for 3 hours in a preheated thermostat oil bath. After the heating period, the autoclave was cooled with ice water. The mixture was transferred to a liquid-liquid extractor to be extracted continuously with 5 × 20 mL chloroform to get rid of nitrobenzene reduction product and any excess of nitrobenzene. The oxidation mixture was acidified by concentrated HCl to pH 3-4 and further extracted with 4 × 15 mL chloroform. The solvent from the second chloroform solution was removed by using rotary evaporator at 40°C under reduced pressure to obtain the nitrobenzene oxidation mixture. The mixture was then dissolved in dichloromethane and made up to 10 mL. This mixture was used as a stock solution for further analysis of the oxidation mixture [13,17].

High performance liquid chromatography (HPLC) was used to analyze the nitrobenzene oxidation mixture. The stock solution (0.2 mL) was pipetted into a 25 mL volumetric flask and made up to volume with acetonitrile-water (1:2 v/v). The resulting sample solution was filtered through a 0.45 μm membrane filter (Millipore) to remove high-molecular weight contaminant. 3,4,5-trimethoxybenzadehyde was used as an internal standard. Next, about 20 μL of the filtrate was injected into the HPLC system (Shimadzu model LC-10AD VP) equipped with a 5 μm Hypersil BDS $C_{18}$ column (25 mm × 4.6 mm i.d.) to determine the quantitative oxidation product. A mixture of acetonitrile-water (1:8 v/v) containing 1% acetic acid was used as an eluent at a flow rate of 2 mL/min and the eluent monitored with a UV detector at 280 nm [13].

Ash and moisture contents were determined according to ASTM-D 1102-56 student procedure. Calculation and the percentage of ash content and moisture contents based on the weight of the moisture-free sample are [18]:

$$\text{Ash content, \%} = (W_2/W_1) \times 100$$

$$\text{Moisture content \%} = (W_1/W) \times 100$$

Where, $W$ = Weight of sample
$W_1$ = Weight of oven-dry sample
$W_2$ = Weight of ash

The molecular weight distribution of the lignin was determined using gel permeation chromatography (GPC) on a PLgel 5 μ Mixed-D column. Monodisperse polystyrene was used as the standard. The sample (100 μL) with a concentration of 1 mg/mL was injected into the GPC. The column temperature and eluent flow rate were set at 40°C and 1 mL/min, respectively.

## 3.0 RESULTS AND DISCUSSION

Table 1 indicates the average yield from three trials of soda lignin isolated at three fractions (pH 2, pH 4 and pH 6) from the black liquor, which was stored at room temperature (24-27°C) and refrigerator temperature (2-5°C). It could be seen that the lignin yields at fractions pH 2 and pH 4 were not influenced by the storage temperatures with pH 2 (0.90-1.00 g/75 mL black liquor) registering a relatively higher yield than pH 4 (0.77-0.83 g/75 mL black liquor). This is speculated as due to the relatively higher $H^+$ ions at pH 2 that were introduced into black liquor, which will be able to react with the –OH groups from the lignin compounds, hence increasing the possibilities for precipitation. This is further proven by the lignin yield at fraction pH 6, which showed the lowest yield (<0.59/75 mL black liquor) as compared to the other two fractions.

It was observed that only trace amount or none of the lignin was isolated at pH 6 for 60th and 90th day from the black liquor stored at room temperature. This phenomenon is probably due to the higher rate of biodegradation activities in the lignin compound at room temperature. Also, the yields of lignin (at pH 6) are generally lower with

**Table 1** The average (3 trials) yield of lignin precipitated by 10% v/v hydrochloric acid until pH 2, pH 4 and pH 6 in g/75 mL black liquor

| **Storage condition** | **Fraction** | **5th day** | **15th day** | **30th day** | **60th day** | **90th day** |
|---|---|---|---|---|---|---|
| At room temperature (24-27°C) | pH 2<br>pH 4<br>pH 6 | 0.97 ± 0.02<br>0.81 ± 0.01<br>0.45 ± 0.01 | 0.90 ± 0.01<br>0.78 ± 0.02<br>0.56 ± 0.01 | 0.90 ± 0.03<br>0.81 ± 0.02<br>0.56 ± 0.02 | 0.91 ± 0.02<br>0.77 ± 0.02<br>Trace | 0.99 ± 0.01<br>0.82 ± 0.02<br>Trace |
| Storage in refrigerator (2-5°C) | pH 2<br>pH 4<br>pH 6 | 0.98 ± 0.03<br>0.82 ± 0.02<br>0.59 ± 0.03 | 0.94 ± 0.01<br>0.83 ± 0.02<br>0.57 ± 0.02 | 0.95 ± 0.02<br>0.82 ± 0.01<br>0.48 ± 0.01 | 0.92 ± 0.02<br>0.78 ± 0.01<br>0.35 ± 0.03 | 1.00 ± 0.02<br>0.81 ± 0.02<br>0.34 ± 0.02 |

storage time, which is due to the degradation of higher molecular lignin structures and also co-precipitation of non-lignin compounds during longer storage period. Under condition of constant storage time, the biodegradation activity of the black liquor was higher at room temperature as compared to cool temperature. The results of this study suggest that the storage time for the black liquor regardless of the storage temperature is 15 days or less.

Alkaline nitrobenzene oxidation is one of the standard chemical degradation methods that can be used for lignin determination. The resulting oxidative products were then analyzed by high performance liquid chromatography (HPLC). In the case of soda lignin, three constitutive monomeric units, which are *p*-hydroxyphenyl, guaiacyl and syringyl will produce the corresponding *p*-hydroxybenzaldehyde, vanillin and syringaldehyde. A typical HPLC chromatogram for soda lignin from black liquor of oil palm EFB is shown in Figure 1. The major compounds found in this lignin sample are tabulated in Table 2 against their retention times as recorded in Figure 1.

**Table 2** Main compounds present in a typical soda lignin from black liquor of oil palm EFB fibers sample

| Compound | Retention time (minutes) |
|---|---|
| *p*-hydroxybenzoic acid | 6.100 |
| Vanillic acid | 7.900 |
| Syringic acid | 8.550 |
| *p*-hydroxybenzaldehyde | 10.375 |
| Vanillin | 13.125 |
| Syringaldehyde | 15.092 |

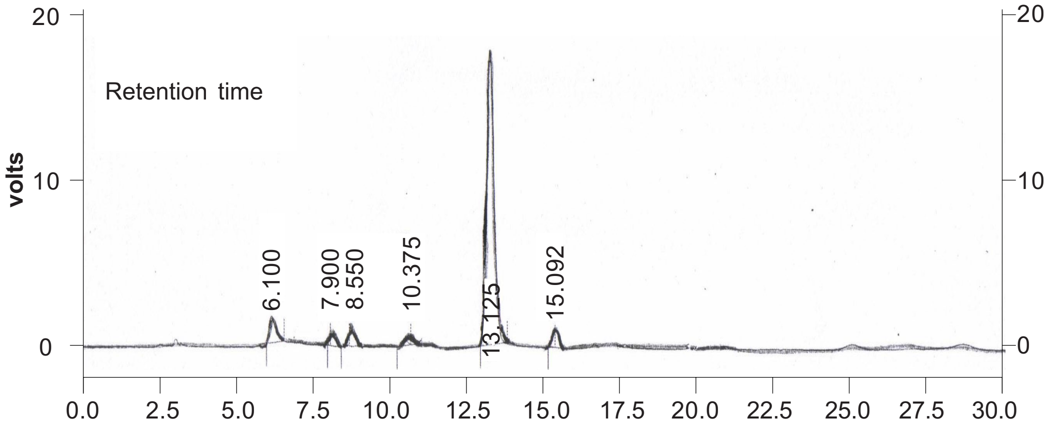

**Figure 1** Typical HPLC chromatogram for soda lignin from black liquor of oil palm EFB fibers

The percentage of alkaline nitrobenzene oxidation products of lignin at pH 2, pH 4 and pH 6 at different storage temperatures is shown in Table 3. For both storage temperatures, the predominant product was vanillin comprising of 44.9-52.1% of the total product. Syringaldehyde was a second major product, which is about 21.5-30.8%, followed by *p*-hydroxybenzaldehyde (6.8-14.3%). Neither *p*-coumaric acid nor ferulic acid has been detected in the oxidation mixtures, which was suspected to have been oxidized into *p*-hydroxybenzaldehyde or *p*-hydroxybenoic acid [17] and vanillin or vanillic acid [12], respectively under the nitrobenzene oxidation condition given.

**Table 3** Percentage of nitrobenzene oxidation product of lignin at different pH and storage conditions

| | | Storage at room temperature (24-27°C) | | | | | | Storage in refrigerator (2-5°C) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Days** | **Fraction** | **PHBA** | **VA** | **SYA** | **PHBAL** | **VAN** | **SYAL** | **PHBA** | **VA** | **SYA** | **PHBAL** | **VAN** | **SYAL** |
| 5th | pH 2 | 0.1 | 1.4 | 4.0 | 8.4 | 51.0 | 28.2 | T | 2.6 | 8.6 | 9.5 | 50.8 | 23.1 |
| | pH 4 | T | 1.8 | 4.9 | 7.7 | 49.8 | 30.8 | 0.1 | 1.7 | 5.5 | 7.4 | 50.6 | 29.2 |
| | pH 6 | 0.1 | 1.4 | 4.0 | 8.4 | 51.0 | 28.2 | T | 2.6 | 8.6 | 9.5 | 50.8 | 23.1 |
| 15th | pH 2 | 0.2 | 2.1 | 8.4 | 8.2 | 50.4 | 26.1 | 0.2 | 1.8 | 7.8 | 8.6 | 52.1 | 25.4 |
| | pH 4 | 0.1 | 2.2 | 9.3 | 6.9 | 50.9 | 25.7 | T | 2.3 | 8.3 | 8.1 | 50.6 | 26.9 |
| | pH 6 | 0.1 | 2.5 | 9.2 | 6.8 | 51.6 | 24.6 | 0.3 | 2.3 | 8.2 | 7.7 | 51.2 | 27.2 |
| 30th | pH 2 | 0.1 | 1.7 | 6.7 | 11.7 | 46.9 | 25.2 | 0.1 | 1.6 | 7.0 | 11.5 | 48.2 | 25.2 |
| | pH 4 | T | 1.9 | 6.6 | 10.2 | 46.5 | 24.2 | 0.1 | 1.7 | 6.9 | 10.6 | 49.0 | 26.1 |
| | pH 6 | 0.4 | 1.6 | 6.2 | 12.6 | 48.8 | 21.5 | 0.3 | 1.7 | 6.8 | 12.1 | 50.5 | 23.1 |
| 60th | pH 2 | 0.3 | 2.0 | 8.6 | 10.0 | 49.5 | 25.5 | 0.4 | 2.3 | 9.7 | 8.1 | 50.1 | 26.7 |
| | pH 4 | 0.1 | 2.0 | 8.1 | 8.4 | 48.7 | 25.3 | 0.3 | 2.0 | 8.9 | 7.7 | 50.7 | 26.8 |
| | pH 6 | N/A | N/A | N/A | N/A | N/A | N/A | 0.5 | 1.9 | 7.1 | 10.1 | 50.5 | 24.3 |
| 90th | pH 2 | 0.8 | 0.9 | 8.3 | 10.7 | 44.9 | 26.8 | 0.5 | 2.0 | 9.6 | 10.1 | 49.7 | 25.2 |
| | pH 4 | 0.1 | 1.7 | 6.7 | 14.3 | 48.5 | 23.4 | 0.3 | 2.3 | 9.0 | 9.9 | 48.9 | 24.3 |
| | pH 6 | N/A | N/A | N/A | N/A | N/A | N/A | 0.7 | 1.9 | 9.2 | 12.0 | 50.0 | 24.7 |

*p*-hydroxybenzoic acid=PHBA, Vanillic acid=VA, Syringic acid=SYA, *p*-hydroxybenzaldehyde=PHBAL, Vanillin=VAN, Syringaldehyde=SYAL, Trace=T and Not Available=N/A

Table 4 presents the moisture and ash contents of the isolated lignin. Lignin is a hygroscopic compound due to the presence of –OH groups in the molecule, which cause the lignin to absorb moisture from the atmosphere. It was found that generally, the moisture and ash contents of fraction pH 6 were the highest compared to the pH 2 and 4 fractions especially at longer storage time. This phenomenon is probably due to the presence of non-dissolving non-lignin materials such as polysaccharide and precipitated silica, which otherwise would have been dissolved at lower pH.

**Table 4** Moisture and ash contents of soda lignin at three pH fractions isolated by hydrochloric acid from black liquor at different storage times and temperature conditions

| **Days** | **Fractions** | **Storage at room temperature (24-27°C)** | | **Storage in refrigerator (2-5°C)** | |
|---|---|---|---|---|---|
| | | **Moisture content, %** | **Ash content, %** | **Moisture content, %** | **Ash content, %** |
| 5th | pH 2 | 5.53 | 0.64 | 5.50 | 0.42 |
| | pH 4 | 5.58 | 3.06 | 6.05 | 0.94 |
| | pH 6 | 6.77 | 5.32 | 8.62 | 7.63 |
| 15th | pH 2 | 6.50 | 1.66 | 5.41 | 1.66 |
| | pH 4 | 5.27 | 1.44 | 6.37 | 4.67 |
| | pH 6 | 5.98 | 4.34 | 8.54 | 4.24 |
| 30th | pH 2 | 5.84 | 2.69 | 8.22 | 0.53 |
| | pH 4 | 6.37 | 0.74 | 6.93 | 1.38 |
| | pH 6 | 9.65 | 5.25 | 9.14 | 3.80 |
| 60th | pH 2 | 6.80 | 2.57 | 7.41 | 1.75 |
| | pH 4 | 8.25 | 6.18 | 5.95 | 4.82 |
| | pH 6 | N/A | N/A | 14.25 | 14.85 |
| 90th | pH 2 | 6.48 | 4.86 | 5.64 | 1.50 |
| | pH 4 | 8.89 | 6.56 | 9.45 | 6.59 |
| | pH 6 | N/A | N/A | 11.34 | 8.93 |

## 4.0 CONCLUSIONS

From this study, based on the percentage of yield and the degree of purity, the most suitable pH value to precipitate soda lignin from black liquor of oil palm EFB is pH 2. Nitrobenzene oxidation analysis showed that, the predominant compound in the soda lignin was vanillin, followed by syringaldehyde and *p*-hydroxybenzaldehyde. Storage time for the black liquor of more than 15 days should be avoided to prevent high rate of biodegradation activities, which will result in lower lignin yield.

Although nowadays lignin can easily be obtained from trees, this project was aimed for two major purposes, which are to overcome problems due to the oil palm wastes and at the same time to recycle the unwanted materials into a valuable product. Due to low yield percentage, some serious efforts are needed in order to improve the isolation technique of lignin from black liquor. Recently, with higher demands for the EFB as a new material for pulp and paper production, obtaining lignin from black liquor may not be a bad idea for commercial purposes in the near future.

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