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## Lignin preparation from oil palm empty fruit bunches by sequential acid/alkaline treatment – A biorefinery approach



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### HIGHLIGHTS

- OPEFB fibers has a good potential as raw material for lignin preparation.
- The lignin obtained present a high industrial potential as precursor of biocomposites.
- The acid pretreatment using 1% (w/w) of H<sub>2</sub>SO<sub>4</sub> at 121 °C and 60 min hydrolyzed 80% of hemicellulose.
- The lignin extraction was 68.8% (w/w) of the original lignin in cell walls at 2.5% (w/w) NaOH, 80 min and 121 °C.
- Degradation products and excessive depolymerization by this method were detected using FTIR and NMR.

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### ABSTRACT

Lignin is an important raw material for the sustainable biorefineries and also the forerunner of high-value added products, such as biocomposite for chemical, pharmaceutical and cement industries. Oil palm empty fruit bunches (OPEFB) were used for lignin preparation by successive treatment with 1% (w/w) H<sub>2</sub>SO<sub>4</sub> at 121 °C for 60 min and 2.5% NaOH at 121 °C for 80 min resulting in the high lignin yield of 28.89%, corresponding to 68.82% of the original lignin. The lignin obtained was characterized by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The results indicated a lignin with molecular masses ramping from 4500 kDa to 12,580 kDa. FTIR and NMR of these lignins showed more syringyl and *p*-hydroxyphenyl than guaiacyl units. Moderate acid/alkaline treatment provided lignin with high industrial potential and acid hydrolyzates rich in fermentable sugars and highly porous cellulosic fibers.

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### 1. Introduction

Oil palm (*Elaeis guineensis*) is a dominant agricultural crop in many countries, Malaysia and Indonesia being the two largest growers and producers of oil palm. They altogether account for roughly 85% of the world oil palm production representing 53,500 million tonnes (Mohammed et al., 2012; Singh et al., 2013; Tan et al., 2013). In South America, Brazil is the third largest producer after Colombia and Ecuador, producing 340 million tonnes, representing 0.58% of the worldwide oil palm production (data from: 'www.indexmundi.com', 2015 accessed: 13-04-2015). However, Brazil has a potential area to cultivate oil palm in roughly

70 million of hectares, which may become one of the largest producer.

In tandem with oil production, the solid by-product oil palm empty fruit bunches (OPEFB) are generated. OPEFB are the fibrous mass left behind after separating the fruits from sterilized (steam treatment at 294 kPa for 1 h) fresh fruit bunches (FFB) (Shinoj et al., 2011). It is estimated that for each tonne of oil palm produced, about 1.1 tonnes of OPEFB are generated. In 2011, the world production was 14.5 million tonnes (dry basis), half of it being produced in Indonesia (Purwandari et al., 2013).

The OPEFB has been used traditionally as source of heat and power in incinerators of palm oil mills, causing environmental pollution (Cotana et al., 2014). Nevertheless, OPEFB can serve as a renewable source of sugar and lignin, available in large amounts and at relatively low costs for chemical and fuels, through the biorefinery approach (Wildschut et al., 2013).

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In a biorefinery, the lignin can be converted to high-value-added chemicals such as, resin precursors, antioxidants, antimicrobial agents, aromatics compounds, synthetics alcohols, Fisher–Tropsch liquid fuel, syngas, and molecules of high and low molecular weight, which can be profitable. Lignin is considered of utmost importance to achieve sustainable economy and to reduce carbon footprint (Azadi et al., 2013; Chew and Bhatia, 2008).

The extraction of lignin can be done using various methods such as, organosolv, acid-isolation, alkaline-isolation, Kraft process and ionic liquids. Nonetheless, these separation methods are generally expensive and/or require extreme temperature and pressure, which are not easy to apply at industrial scale production (except Kraft carried out in pulp and paper from wood). Therefore, an efficient and inexpensive method is necessary for extraction of lignin from lignocellulosic biomass.

In this work, the lignin extraction from oil palm empty fruit bunches was carried out through sequential acid/alkaline treatment. The acid pretreatment was carried out using a fixed concentration of  $H_2SO_4$ , whereas, the alkaline lignin extraction was performed by varying NaOH concentration and time of reaction. The black liquor resulting from alkaline treatment of OPEFB was processed lowering the pH to obtain lignin. The mass yield of lignin extraction was designed as the variable to determine the best conditions of lignin extraction from OPEFB. The chemical quality of lignin extracted was analyzed by comprehensive set of analytical methods, including gas permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR),  $^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR). The morphology of OPEFB fibers after each pretreatment was studied by scanning electron microscopy (SEM).

## 2. Lignin structure

The exact structure of lignin remains virtually unknown, however it is known and acceptable that basic chemical structure is composed of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), *p*-coumaryl, coniferyl and sinapyl alcohols (Lin and Dence, 2007). These alcohols are converted to *p*-hydroxyphenyl, guaiacyl and syringyl respectively by enzymatic reactions. The presence of each monomer varies in every sort of biomass, for example, gymnosperm lignin is formed mostly by guaiacyl, angiosperm lignin by guaiacyl and syringyl units, while grass lignin is composed of guaiacyl, syringyl and *p*-hydroxyphenyl units. The polymerization of these monomers is catalyzed by laccase and/or peroxidase via radical coupling of their corresponding phenoxy radicals, forming the aliphatic and aryl ether linkages at C- $\alpha$  and C- $\gamma$ , ester linkages at C- $\gamma$  and  $\beta$ -O-C(4), resulting in a complex tree dimensional polymeric structure, being the two major ether bonds the  $\beta$ -O-C(4) and  $\alpha$ -O-C(4) (Cyril et al., 2010).

## 3. Methods

### 3.1. Lignocellulosic biomass

Oil palm empty fruit bunches (OPEFB) were obtained from Biopalm Vale factory, located in Mojú, Pará state of Brazil. The OPEFB was dried in a cross flow stove at 65 °C by for 48 h, milled in mill knives and sieved, through a mesh 42 (0.350 mm) screen and used for all experiments. All experiments were carried out in triplicates.

### 3.2. Sequential acid/alkaline pretreatment for lignin extraction

Acid hydrolysis treatment was carried out according to the procedure reported by Minu et al. (2012). Briefly, about 6 g of dry

OPEFB fibers were weighed into a flask with 53.4 ml of distilled water, and 452.9  $\mu$ l (72% v/v) sulfuric acid was added as catalyst. This volume ratio represents in terms of mass percentage: 10%, 89% and 1% (w/w) of OPEFB, water and sulfuric acid, respectively. The temperature of autoclave was fixed at 121 °C and reaction time was 60 min.

The acid treated OPEFB was washed three times with distilled water and dried overnight at 80 °C. Later, alkaline lignin extraction was carried out. In a flask, 3 g of dry OPEFB were mixed with different volumes of 5 M NaOH and distilled water, obtaining solutions of 10% (w/w) OPEFB, 0.5% (w/w) to 5.5% (w/w) of NaOH and the volume made up by distilled water. The mixture was incubated at 121 °C in an autoclave, with the aim to analyze the effect of NaOH on lignin extraction. The reaction time was fixed at 60 min.

The yield of lignin extraction was determined as a function of NaOH mass percentage in solution. The global mass yield of lignin extraction ( $G_{Y_l}$ ) and the specific lignin yield extraction ( $E_{Y_l}$ ) are presented in Eqs. (1) and (2).

$$G_{Y_l} = \frac{M_l}{M_t} 100 \quad (1)$$

$$E_{Y_l} = \frac{M_l}{M_t^i} 100 \quad (2)$$

where  $M_l$  is the mass of lignin obtained,  $M_t$  is the total mass of OPEFB,  $M_t^i$  is the mass of acid insoluble lignin present in OPEFB after acid treatment.

The best condition, in terms of NaOH mass percentage in solution, was determined at the point in which the highest yield was achieved. This condition was selected to analyze the effect of reaction time, varying from 40 min to 120 min, while the temperature was maintained at 121 °C.

The precipitation of lignin was conducted overnight using (72% v/v)  $H_2SO_4$  at pH 2.0. At higher pH values, precipitation was not detected, as reported by Minu et al. (2012). Whatman No. 4 filter paper was employed for vacuum filtration. The filtered liquid was analyzed for cellulose, hemicellulose and acid soluble lignin, as described in the Section 3.3.

The solid fraction so obtained, was washed three times with acid water for removal of carbohydrates and impurities. The excess acid was washed three times with hot water at 40 °C for 30 min. Finally, the solid lignin was vacuum dried for 8 h at 35 °C and stored at room temperature in a flask covered with foil.

### 3.3. Analysis of carbohydrates and total lignin

The composition of polysaccharides was determined using the NREL analytical procedure reported by Sluiter et al. (2011). The cellulose (Cel) and hemicellulose (Hem) mass composition were obtained using the equations reported by Tan et al. (2013), correlating the concentration of glucose (Gluc), xylose (Xyl) and arabinose (Arab), acquired from High-Performance Liquid Chromatography (HPLC), in a Shimadzu Chromatograph equipped with an Aminex HPX-87H column, working in a furnace at 60 °C. Mobile phase was sulfuric acid (5 mM) at rate of 6 ml  $min^{-1}$  with an IR detector.

The acid soluble lignin (ASL) and acid insoluble lignin (AIL) were determined following NREL procedure (Sluiter et al., 2011). The acid soluble lignin was measured by absorbance of liquid hydrolyzate at 280 nm with dilution factor of 10, while the acid insoluble lignin is defined as the Klason lignin ash free.

### 3.4. Gel permeation chromatography (GPC)

The determination of molecular weight and polydispersity of extracted fraction lignin was carried out by GPC analysis in a

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