



Characterization of syringyl and guaiacyl lignins in thermomechanical pulp from oil palm empty fruit bunch by pyrolysis-gas chromatography-mass spectrometry using ion intensity calibration



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ABSTRACT

Thermomechanical pulp (TMP) was fabricated from the empty fruit bunch (EFB) of oil palm (*Elaeis guineensis*) by using a laboratory-scale pressurized refiner. The EFB TMP was separated by screens (850, 355, and 180 μm openings) into four fractions. Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) indicated analogous chemical features of lignin in the TMP fractions by determining eight pyrolysis products from its syringyl (S) and guaiacyl (G) types. The amount of each pyrolysis product was quantitatively determined through a calibration line obtained by the conversion factor of the main ion intensity to an authentic compound weight. Moreover, S/G molar ratios obtained by Py-GC/MS provided a good correlation with the syringaldehyde/vanillin (S_a/V_a) molar ratios obtained by nitrobenzene oxidation for raw EFB material and some hardwoods. The TMP fabrication process slightly changed the lignin structure. Py-GC/MS was found to be a reliable analytical method for the characterization of lignin in EFB TMP.

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1. Introduction

Oil palm (*Elaeis guineensis*) is cultivated in West and Central Africa, where it originated, and is one of the largest commercial crops in Malaysia, Indonesia, and Thailand. However, the empty fruit bunch (EFB) of oil palm also has many negative impacts on the biodiversity and the environment (Obidzinski et al., 2012). Moreover, global production of paper and paperboard has increased year by year because of significant growth of the global economy, resulting in a shortage of wood. EFB fibers are abundantly available and could potentially replace wood in a variety of industries. EFB fibers could be useful for preparing paperboard, dissolving pulp, and have other applications in treating agricultural waste (Harsono et al., 2015, 2016).

Development of thermomechanical pulp (TMP) was established in the 1970s. Today, thermomechanical pulping is the most dominant among all mechanical pulping methods (Gorski et al., 2010). In thermomechanical pulping, pressurized steam is introduced to the refining process to soften the lignin of the materials. The main purpose of refining is to apply a mechanical force to the materials in order to separate and fibrillate the fibers, which is achieved by removing the middle lamella from the cell walls (Li et al., 2011).

In addition to paperboard production, dried fibers of EFB TMP are useful in medium-density fiberboard (MDF) as an alternative to wood. In previous studies, TMP was successfully obtained from raw EFB material by dry- and wet-blowing methods, and the paper properties of the pulp were clarified (Mulyantara et al., 2016a,b). However, the characteristics of lignin chemical feature which should affect bleaching ability and paper properties for EFB TMP have not yet been clarified.

Nitrobenzene oxidation (NBO) has been widely used to study the characteristics of lignin structures (Chen, 1992; Nishimura et al., 2002; Claudio et al., 2008). Syringaldehyde (S_a) and vanillin (V_a), the main aromatic aldehydes, are obtained from lignin by NBO. S_a and V_a represent the non-condensed structures of lignin, whereas

Abbreviations: EFB, empty fruit bunch; TMP, thermomechanical pulp; Py, GC/MS pyrolysis-gas chromatography-mass spectrometry; NBO, nitrobenzene oxidation; S, syringyl; G, guaiacyl; S_a , syringaldehyde; V_a , vanillin.

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the condensed structures of carbon–carbon linkages between the side chains and the aromatics of lignin do not form S_a and V_a . Cupric oxide oxidation and NBO with organic solvent extraction and gas chromatography (GC) are very time consuming and chemically consuming for lignin characterization. Thus, pyrolysis–gas chromatography (Py–GC) has been recommended as an alternative analytical method because it is faster, safer, and more economical than other methods (Kuroda et al., 2005a; Claudio et al., 2008).

Analytical pyrolysis has been widely applied to the characterization of lignocellulosic materials (Galletti and Bocchini, 1995; Moldoveanu 1998; Yokoi et al., 1999; Kuroda and Nakagawa-Izumi, 2005b; Alves et al., 2006). This method incorporates Py–GC with a flame ion detector (FID) and Py–GC/mass spectrometry (MS) (Faix et al., 1988; Kleen et al., 1993; Sjoberg et al., 2002; Rencoret et al., 2009).

Py–GC/MS analysis of various hardwood materials gives a good relationship in syringyl/guaiacyl (S/G) and syringaldehyde/vanillin (S_a/V_a) ratios between Py–GC/FID and GC analysis of the NBO products (Izumi et al., 1995). However, the reliability of Py–GC/MS using total ion (TI) intensity to obtain a similar relationship between the Py–GC/MS and the NBO method has not been clarified yet. S/G and S_a/V_a molar ratios are important indicators of the reactivity of lignin (Ibarra et al., 2005; Rovia et al., 2011), and they have been roughly calculated from the TI response of selected S- and G-type products (Lima et al., 2008; Nunes et al., 2010).

In this study, lignin in EFB TMP was characterized by Py–GC/MS and NBO to better understand the structural changes of TMP long fibers and fines in the process. First, fractions of TMP long fibers and fines were compared, and then the reliability of Py–GC/MS as a method of analyzing the syringyl and guaiacyl structures was clarified.

2. Experimental

2.1. Material

Oil palm EFB was obtained from PT. Madukismo in Yogyakarta, Indonesia, and PT. Perkebunan Nusantara VIII in Bogor, West Java, Indonesia. The materials, which had a 10% moisture content, were cut into lengths of 0.4–0.5 cm by a laboratory disk mill for preparing thermomechanical pulping. Japanese hardwoods materials (*Pupulus sieboldii*, *Quercus myrsinaeforia*, *Quercus crispula*, *Castanopsis cuspidate*, and *Aesculus turbinata*) were provided by the Forestry and Forest Products Research Institute, Tsukuba, Japan. The materials were milled into particles (60–80 mesh size) for acetone extraction and chemical analysis.

2.2. TMP fabrication and dry fractionation with screens

EFB TMP was made at 160 °C using the dry-blowing method according to a procedure previously reported (Mulyantara et al., 2016b). The dried TMP fibers and fines were separated into four fractions using screens with 850, 355, and 180 μm openings (20, 45, and 80 mesh, respectively). Approximately 10 g of dried TMP was placed into the upper screen (850 μm opening) with 30 stainless steel balls (12.5 mm diameter) to disperse the fibers so that they dropped smoothly in subsequent screens during shaking for 2 min. These four fractions were denoted as “On 850 μm opening,” “850–355 μm opening,” “355–180 μm opening,” and “Pass 180 μm opening.”

2.3. Analysis of chemical composition for EFB materials and TMP

The contents of acid-insoluble lignin, acid-soluble lignin, extractives, and ash were determined using TAPPI Test Methods T 222 om-15 (TAPPI, 2015), T 204 cm-07 (TAPPI, 2007), and T 211 om-02

(TAPPI, 2002). The amount of glucose, xylose, and others sugars in the acid hydrolysate of materials and TMP were determined using ion chromatography (Harsono et al., 2016).

2.4. Py–GC/MS

2.4.1. Making calibration lines of lignin pyrolysis products using main ion intensity (MI)

The conditions of Py–GC/MS were as follows: Pyrolyzer, JHP-5 (Japan Analytical Industry Co. Ltd. Japan); pyrolysis conditions, 500 °C for 4 s; GC/MS system, QP-5050A (Shimadzu, Japan); column, HP 1-MS (30 m \times 0.25 mm; film thickness: 1.0 μm). Temperature profile for GC analysis: 1 min at 50 °C, 50–280 °C (at a rate of 5 °C/min), and 13 min at 280 °C. Approximately 150–180 μg of each sample prepared with *n*-eicosane (0.1 μg) as an internal standard (IS) was placed on a ferromagnetic pyrofoil and tightly wrapped (Geib et al., 2008). Then, the sample-loaded pyrofoil was inserted into a quartz sample tube. The sample holder with the sample tube was centered in the pyrolyzer, and then Py–GC/MS started. The main ion intensity (MI) conversion factors (weight-to-MI area on the chromatogram) for the lignin pyrolysis products were obtained by making calibration lines between the weight and area ratios of commercial monomeric lignin model compounds and the internal standard. Approximately 15 mg of each compound was dissolved in 50 mL of ethanol. Calibration lines were created by injections of various amounts of the compound with 0.1 μg of IS. Three replicas were performed for each sample.

2.4.2. Determination of lignin pyrolysis product yields and S/G molar ratios

The amount of each lignin pyrolysis product was determined using the MI conversion factor of the product. The yields, which were based on the weight of the prepared sample (or its acid-insoluble lignin content) and the S/G molar ratio, were then evaluated.

2.5. Nitrobenzene oxidation

According to a modified NBO method (Chen, 1992), approximately 200 mg (oven-dried weight) of the prepared sample, 7.0 mL of 2 N NaOH, and 0.4 mL of nitrobenzene (chemical analysis pure grade) were placed together in a 10 mL steel reactor and oxidized at 170 °C for 2 h. Then, ethyl vanillin (2 mg) as an internal standard was added to the reaction mixture. The mixture was extracted three times using 20 mL of ether. The lower (water) layers of the mixture were gathered and acidified to pH 3–4 using 2 N HCl. The mixture was again extracted three times using 25 mL of ether. The upper (ether) layers were gathered and washed with 5 mL of water to remove the remaining acid. Then, approximately 20 g of anhydrous Na_2SO_4 was added to the collected ether layers, and the ether fraction was stored for 24 h. After filtration of the mixture, the ether was evaporated. S_a and V_a were concentrated and ready for GC. Above procedures of each sample were done for three replicas.

The conditions for GC equipped with FID were as follows: GC system, GC-17A (Shimadzu, Japan); column, DB-1 (30 m \times 0.25 mm; film thickness: 0.25 μm) with helium gas as a carrier. Temperature profile for analysis: 15 min at 110 °C, 110–160 °C (at a rate of 5 °C/min), 160–280 °C (at a rate of 20 °C/min), and 7 min at 280 °C. The FID response factors for estimating the amount of S_a and V_a were obtained by making calibration lines between the weight ratios and area ratios of S_a and V_a to the internal standard. Calibration lines were created by injection with various concentrations of the compound (approximately 2, 4, and 2 mg/mL) with the internal standard (2, 1, and 0.2 mg/mL). The amounts of S_a and V_a and the

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