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A Comparative Study of Oil Palm and Japanese Beech on their Fractionation and Characterization as Treated by Supercritical Water

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Abstract

Supercritical water treatment (380ºC/100MPa/8s) was applied to extractives-free oil palm trunk and sapwood portion of Japanese beech and their fractionated products were comparatively characterized, for water-soluble portion and water-insoluble portion composed of methanol-soluble portion and methanol-insoluble residue. As a result, the water-soluble portion was determined to be composed of carbohydrate-derived products such as organic acids, sugar decomposed products and lignin-derived products, etc. for both species. The oil palm, however, shows higher yield of organic acids and lignin-derived products compared to Japanese beech. The methanol-soluble portion was, on the other hand, mainly composed of lignin-derived products, and in oil palm, these lignin-derived products consisted of both syringyl and guaiacyl-type similar to Japanese beech. The methanol-insoluble residue, was also mainly composed of lignin to be 99.2% in its content in the oil palm, compared to

Japanese beech 93.7%. Moreover, the phenolic hydroxyl content determined by aminolysis method was higher in oil palm (36.5 PhOH/100C_9) compared to Japanese beech (16.9 PhOH/100C_9). Furthermore, an alkaline nitrobenzene oxidation analysis indicated that, the methanol-insoluble residue of the oil palm was less in oxidation products whereas in Japanese beech nitrobenzene oxidation products completely diminished. These lines of evidence suggest that methanol-insoluble residue is composed of lignin with more condensed-type of linkages with high phenolic hydroxyl groups. In addition, the water-soluble portion could be utilized for organic acid production, whereas the methanol-soluble portion and its insoluble residue for phenolic chemical production.

Keywords: supercritical water treatment; oil palm; Japanese beech; carbohydrate-derived products; lignin-derived products; organic acid production; phenolic chemical production

1. Introduction

Biomass shows a great potential for the production of renewable transportation fuels and chemicals. Biomass is extremely abundant resource that can be produced in agriculture, forestry and also collected as waste residues. Therefore, efficient utilization of biomass is a significant challenge for meeting the future fuel and chemical needs. For conversion of lignocellulosic biomass into fuel ethanol, however, certain challenges need to be addressed such as requirement for an efficient microorganism that is able to ferment a variety of sugars (pentoses and hexoses) [1], regulations against genetically modified organisms [2] and also challenges in producing the fuel ethanol economically. Therefore, conversion of lignocellulosic biomass into other chemicals is preferred.

Meanwhile, supercritical water treatment (>374ºC, >22.1MPa) is a clean process that is preceded without a catalyst and for a short reaction time. It has been applied to hydrolysis of cellulose [3] and wood [4, 5] for potential recovery of saccharides, dehydrated and fragmented compounds as well as organic acids and lignin-derived phenolic compounds.

In the present study, two biomass samples have been selected because of their anatomical differences, which are oil palm (*Elaeis guineensis*) and Japanese beech (*Fagus crenata*). Under botanical terms, oil palm is classified as one of monocotyledonous angiosperms, whereas Japanese beech, a hardwood, is classified as one of dicotyledonous angiosperms. In oil palm, vascular bundles, which consist of both xylem and phloem are scattered throughout the trunk. Whereas, in sapwood portion of hardwoods, it only consists of secondary xylem. As such, it implies that oil palm has distinct characteristics in comparison to hardwoods and therefore needs to be investigated further. With huge land coverage of oil palm especially in Indonesia, Malaysia and Thailand, a large amount of the oil palm trunk is generated annually as a result of replantation after the average height of the plant exceeds 10m. It is estimated that in the year 2004 alone, 5Mton of oil palm trunk was generated in Malaysia [6]. Meanwhile, Japanese beech is generated as waste wood chips. Therefore, this study will also enable us to investigate the future potential utilization of these biomass samples.

2. Materials and Methods

2.1 Sample preparation

The oil palm trunk was obtained from Johor Bahru, Malaysia, while sapwood portions of Japanese beech was from Kyoto, Japan. These samples were first cleaned and air-dried. The air-dried samples were then pulverized using a Wiley mill (Yoshida Seisakusho, Japan) and a Fritsch mill (Fritsch, Germany) to pass through 70-mesh sieves. The pulverized samples were then extracted with ethanol/benzene (1:2, v/v) for 8h in a Soxhlet apparatus. Subsequently these samples were oven-dried at 105ºC for 10h prior to use for experiments.

2.2 Determination of chemical composition in biomass samples

Prior to the supercritical water treatment, chemical composition of those 2 biomass samples were determined. Extractives-free biomass flour was used for the determination of holocellulose, α-cellulose, lignin and ash contents according to refs. [7-9].

2.2 Supercritical water treatment and fractionation of the products

The supercritical water biomass conversion system used in this study was associated with a batch-type reaction vessel made of Inconel-625 with a volume of 5ml [4]. The extractives-free oven-dried sample (150mg) was placed in the reaction vessel with 4.9ml distilled water of high performance liquid chromatography (HPLC)-grade (Nacalai Tesque Inc., Kyoto). Thermocouple and pressure gauge were attached to the reaction vessel. The reaction vessel was then quickly heated by immersing it into the molten tin bath preheated at 500ºC. After the temperature rising time of about 22s, supercritical water treatment proceeded for 8s, which represented the temperature inside the reaction vessel at an average of 380ºC and pressure at 100MPa during the 8s treatment. After that, the reaction vessel was immersed into water bath to quench the reaction.

Eventually, the supercritical water treated products was refrigerated for 12h and filtrated to separate water-soluble portion and water-insoluble residue. The obtained water-insoluble residue was then washed with 10ml HPLC-grade methanol (Nacalai Tesque Inc., Kyoto) for 10min by sonication. The methanol-insoluble residue was then separated by filtration from methanol-soluble portion as filtrates. Subsequently, the yields of these fractions were determined quantitatively after complete evaporation of methanol from methanol-insoluble residue. The yield of water-soluble portion was then estimated by subtracting the yield of methanol-soluble portion and methanol-insoluble residue from the initial amount of oven-dried sample used (150mg).

2.3 Characterization of the fractionated portions

Characterization of the water-soluble portion was conducted with HPLC, ion chromatography (IC), capillary electrophoresis (CE) and ultraviolet-visible (UV-Vis) spectrophotometer.

The HPLC analysis was carried out to quantify the presence of monosaccharides and decomposed products of saccharides using Shimadzu LC-10A under the following conditions: column; Shodex KS801, flow-rate; 1ml/min, eluent; HPLC-grade distilled water, column temperature; 80ºC. The IC analysis was, on the other hand, carried out to quantify the presence of oligosaccharides and monosaccharides using Dionex ICS-3000 under these conditions: column; CarboPac PA1, column temperature; 35ºC, eluent; gradient-programmed mixture of HPLC-grade distilled water, 0.2M sodium hydroxide and 1.0M sodium acetate, flow-rate; 1.0ml/min.

Meanwhile, the CE analysis was carried out to quantify the presence of low molecular weight organic acids with an Agilent G1600A under the following conditions: column; fused-silica capillary (104cm x 75μmΦ), buffer; cation pH 5.6 (Agilent Co.), voltage; -30kV, temperature; 15ºC, detector; UV_{270nm} and characterization of the lignin-derived products was conducted with a Shimadzu UV-2400 UV-Vis spectrophotometer at the wavelength of 205nm.

Characterization of the methanol-soluble portion was conducted with Hitachi G7000M-M9000 gas chromatography-mass spectrometry (GC-MS) for qualitative analysis of low molecular weight products under these conditions: column; Varian CP-Sil 8CB (30m x 0.25mmΦ), injector temperature; 250ºC, column temperature; 30ºC (1min), 30ºC → 250ºC (5ºC/min increment), 250ºC (10min), carrier gas; helium, flow-rate; 1.5ml/min, emission current; 20μA.

For characterization of the methanol-insoluble residue, the determination of lignin content was conducted according to refs. [7, 10]. These results were compared with lignin content of the untreated 2 biomass samples. The phenolic hydroxyl content was determined by aminolysis method according to the procedure described by ref. [11] to determine the number of phenolic hydroxyl groups over 100 phenylpropane (C_9) units of lignin (PhOH/100C_9); gas chromatography (Shimadzu GC14B) with flame ionization detector (FID) was used for the phenolic hydroxyl content under the following conditions: column; Shimadzu stainless steel packed with 10wt% polyethyleneglycol 20M on 60/80 mesh Shincarbon A (2m x 3mmΦ), column temperature; 180ºC (isothermal), injection port temperature; 230ºC, detector temperature; 250ºC, carrier gas; helium. The average weight of phenylpropane (C_9) unit of lignin in oil palm was estimated by the weight of syringyl-type and guaiacyl-type C_9 units, considering the molar ratio of syringyl to guaiacyl moieties. For Japanese beech, it was based on hardwood data from ref. [12].

The alkaline nitrobenzene oxidation method employed in this study is according to ref. [13], with veratraldehyde (Nacalai Tesque Inc., Kyoto) as the internal standard. In order to quantify the nitrobenzene oxidation products, vanillin acetate, syringaldehyde acetate and *p*-hydroxybenzaldehyde acetate were prepared with the respective reagent grade chemicals (Nacalai tesque Inc., Kyoto). Quantification of nitrobenzene oxidation products was carried out by gas chromatography (Shimadzu GC14B) with FID under the following conditions: column; Shimadzu CBP-5 column (25m x 0.25mmΦ), column temperature; 100ºC (1 min), 100ºC → 270ºC (5ºC/min increment), 270ºC (10min), injection port temperature; 250ºC, detector temperature; 250ºC, carrier gas; helium, flow-rate; 1.5ml/min.

3. Results and Discussion

Table 1 shows chemical composition of oil palm and Japanese beech. The cellulose content in oil palm was lower compared to Japanese beech. Hemicellulose content is higher in Japanese beech than oil palm. Meanwhile, lignin content is higher in oil palm. In contrast, oil palm also shows substantially higher ash content, which indeed help in recycling the elements from the plant to the soil if it is continuously used as mulching material.

3.1 Fractionation of the products

As in Table 2, supercritical water treatment (380ºC/100MPa/8s) was applied to the 2 biomass samples and the obtained yields for fractionated water-soluble portion and water-insoluble residue were investigated. In a previous work [3], a similar study has been carried out on microcrystalline cellulose under the condition of the rising time of 13s to 380ºC in the molten tin bath preheated at 550ºC, followed by the 380ºC/100MPa treatment in the reaction vessel for 2-8s. The treatment condition is little bit different in this study due to the longer rising time in the molten tin bath (500ºC), approximately 22s, to reach 380ºC/100MPa in reaction vessel.

For oil palm, the yield of water-soluble portion was the highest, but similar to those in Japanese beech. It is known that the water-soluble portion consists more carbohydrate-derived products [4], which makes supercritical water treatment more efficient for decomposing the carbohydrate portion than subcritical water treatment. However, the yield of the methanol-soluble portion of the oil palm was lower than the methanol-insoluble residue. This is exactly the opposite of Japanese beech. Generally, the yield of the methanol-insoluble residue and methanol-soluble portion, are all dependent on the type of lignin linkages [4]. However, oil palms possess high ash content in the Klason lignin, which could cause higher methanol-insoluble residue remaining because ash being deposited in the methanol-insoluble residue.

3.2 Characterization of water-soluble portion

Due to the long rising time, approximately 22s, taken for the temperature inside the reaction vessel to reach 380°C before 8s supercritical water treatment was made, neither oligosaccharides nor monosaccharides were detected; only decomposed products of saccharides such as dihydroxyacetone (DA), levoglucosan (LG), furfural (FR), organic acids and so on were detected as in Table 3 apart from lignin-derived products. The yield of unknown products which was determined by subtracting the identified products from the total is also shown.

The products detected in the water-soluble portion are somewhat similar between oil palm and Japanese beech. However, the yield of organic acids in Japanese beech is lower compared to that in oil palm. In oil palm, the yields of organic acids are more than 10%, whereas in Japanese beech, it is lower than 5%. Therefore, oil palm shows greater potential to be converted into organic acids by prolonging the supercritical water treatment at reduced pressure based on the study conducted with Japanese beech [5]. Organic acids are essential for subsequent conversion into methane and biodegradable polymers [5]. It could also be sold directly as a commodity chemical. Meanwhile, the yields of lignin-derived products are higher in the oil palm. It gives an indication that high non-condensed-type lignin might be present in the oil palm. This is discussed more in detail later.

3.3 Characterization of methanol-soluble portion

For the methanol-soluble portion of the 2 biomass samples, GC-MS analysis was performed. The total-ion chromatograms of the methanol-soluble portion obtained by GC-MS analysis are also shown in Figure 1. Based on the GC-MS analysis, the molecular weight (MW), the mass fragmentation pattern obtained by electron ionization and the peaks identified from Figure 1 are shown in Table 4. Identification of the peaks were conducted with the retention times and mass fragmentation patterns compared with those of the authentic compounds. However, peaks Nos. 3, 4 and 5 were determined from the mass fragmentation pattern reported by ref. [14], whereas peaks Nos. 13, 16 17 and 18 were determined from ref. [15]. It could then be elucidated that these identified phenolic compounds must be mainly derived from lignin as indicated by G (guaiacyl-type) and S (syringyl-type) lignins. These compounds become insoluble as oily products when the critical state of water returns to the initial ambient state. Therefore, they are hydrophobic in nature. However, they could be fractionated mainly as the methanol-soluble portion.

From the previous study [4], it was found that in supercritical water, ether linkages are preferentially cleaved and smaller fraction of lignin-derived can be washed out with methanol. As a result, the residue becomes rich in condensed linkages. For the oil palm, it could be observed that the higher peaks detected were mainly from syringyl-type phenolic compounds. This is due to more syringyl-type lignin contained in oil palm, as reported previously [16]. For Japanese beech, as expected, it revealed the peaks of syringyl-type as well as guaiacyl-type phenolic compounds. This represents the nature of hardwoods. Thus, the oil palm shows similarity with hardwoods. Besides that, the methanol-soluble portion shows the potential for many phenolic compounds to be recovered, as treated by supercritical water. Phenolic compounds have great value for the production of resins, surfactants and tanning agents [17-18].

3.4 Characterization of the methanol-insoluble residue

Table 5 shows the lignin content for the methanol-insoluble residue of these 2 biomass samples. It shows the lignin content for oil palm was 99.2%. For Japanese beech, however, it corresponded to 93.7%. This suggests that the methanol-insoluble residue is mostly composed of lignin and thus cellulose and hemicellulose are thought to be degraded to various compounds with low molecular weights as collected to be water-soluble portion shown in Table 3. Lignin is, thus, recovered mainly as the methanol-insoluble residue as well as methanol-soluble portion.

Table 5 also shows the number of the phenolic hydroxyl groups (PhOH) upon $100C_9$ units of lignin for the methanol-insoluble residue of the 2 biomass samples. It is apparent that the methanol-insoluble residue has more phenolic hydroxyl groups than the untreated biomass samples. Previously, it was demonstrated with lignin model compounds that the condensed-type linkages, such as 5-5 linkage was stable during supercritical water treatment, whereas the non-condensed-type ether linkages such as *β*-*O*-4 linkage was easily cleaved by supercritical water hydrolysis [4]. After the cleavage of the non-condensed-type linkages, phenolic hydroxyl groups increase. This explains the reason for the higher phenolic hydroxyl content observed in methanol-insoluble residues and it suggests that many non-condensed-type linkages are cleaved and that the residues are rich in condensed-type linkages. On the other hand, the phenolic hydroxyl content in untreated oil palm shows distinct characteristics in comparison to hardwood, whereby its content is much higher.

As reported previously [14], the molar ratio of syringyl to guaiacyl moieties as measured by that of syringaldehyde to vanillin (S/V) in the oil palm was 3.5 and in Japanese beech it was found to be 2.3. In addition, the yield of oxidation products of the oil palm shows similarity to hardwood Japanese beech which is more than 40% as shown in Figure 2.

In contrast, the methanol-insoluble residue of oil palm shows small presence of nitrobenzene oxidation products whereas in Japanese beech no presence of alkaline nitrobenzene oxidation products was detected, as shown in Figure 2. These results were expected because nitrobenzene oxidation products are mainly derived from the degradation of the non-condensed-type lignin and the fact that most of these linkages are already cleaved under supercritical water treatment as mentioned above. It also suggests that methanol-insoluble residues are rich in condensed-type lignin.

4. Conclusions

The characteristics of oil palm and Japanese beech after fractionation with supercritical water treatment has been presented and compared with each other. Most of the characteristics of the oil palm as one of the monocotyledonous angiosperms are similar to those of hardwood Japanese beech, one of the dicotyledonous angiosperms. However, the oil palm does show some distinct characteristics from hardwood Japanese beech such as higher ash content and higher phenolic hydroxyl content.

Apart from that, supercritical water technology showed the potential as the rapid and nontoxic conversion process of oil palm and Japanese beech into organic acids and the possibility for many phenolic compounds to be recovered. In addition, a good relation was found for further increasing the yield of organic acids in the oil palm by prolonging the treatment time. Although future investigations are needed for this, this study has already revealed a promising method for the conversion of biomass sources from various anatomical origins to be converted into value-added products.

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Table 1 Chemical composition of the extractives-free oil palm and Japanese beech.

	Chemical composition (wt%)				
Sample	Cellulose[1]	Hemicellulose[2]	Lignin[3]	Ash	Others[4]
Oil palm	31.7	34.4	29.6	4.3	0
Japanese beech	35.6	38.0	21.8	0.6	4.0

[1] Cellulose = α-Cellulose; [2] Hemicellulose = Holocellulose – α-Cellulose; [3] Lignin = Klason lignin + acid-soluble lignin; [4] Others = Protein + Starch + Pectin + Losses during acid chlorite method

Table 2 Yields of fractionated water-soluble portion and water-insoluble residue for oil palm and Japanese beech as treated by supercritical water at 380ºC/100MPa/8s.

Sample	Yield (wt%)		
	Water - soluble	Water - insoluble	
		Methanol - soluble	Methanol - insoluble
Oil palm	82.1	7.5	10.4
Japanese beech	75.7	18.1	6.2

Table 3 Yields of products in the fractionated water-soluble portion of oil palm and Japanese beech.

Sample	Water-soluble (wt%)							
	Dihydroxy-acetone	Levo-glucosan	Methyl-glyoxal	Furfural	Acetic acid	Glycolic acid	Lactic acid	Lignin-derived products
Oil palm	5.4	1.1	0.4	0.5	6.4	4.8	1.7	12.2
Japanese beech	7.6	1.4	0.2	0.2	1.4	2.5	0.8	9.8

Table 4 Identified products in the methanol-soluble portion by its mass fragments in GC-MS analyses, as 2 biomass species treated by supercritical water (380ºC/100MPa/8s).

Peak	MW	Major mass fragments	Compound	Origin	Oil palm	Japanese beech
1	124	109, 124, 81	Guaiacol	G		O
2	152	137, 152, 122	4-Ethylguaiacol	G	O	O
3	134	105, 133, 79, 134	2-Methyl-4-vinylphenol	G	O	O
4	148	133, 146, 105, 78, 92	2-Methyl-4-(1-propenyl) phenol	G		O
5	148	132, 147, 105, 78, 92	2-Methyl-4-(1-propenyl) phenol isomer	G		O
6	154	154, 139, 111	Syringol	S	O	O
7		146, 118, 117, 123, 161	unknown		O	O
8		146, 118, 117, 147, 92	unknown		O	O
9		148, 146, 92, 78, 126	unknown			O
10	164	164, 149, 131	*cis*-Isoeugenol	G	O	O
11	164	164, 149, 103, 77	*trans*-Isoeugenol	G	O	O
12	166	151, 166, 123	Acetoguaiacone	G	O	
13	182	167, 182, 168, 153	4-Ethylsyringol	S	O	O
14	180	137, 179, 122	Guaiacylacetone	G		O
15	196	167, 196, 168, 123	4-Propylsyringol	S	O	O
16	194	194, 179, 119, 91, 77	*cis*-4-Propenylsyringol	S	O	O
17	192	192, 131, 105, 90	4-Propynylsyringol	S	O	O
18	194	194, 119, 151, 179, 77	*trans*-4-Propenylsyringol	S	O	O
19	178	178, 135, 108, 77	*trans*-Coniferylaldehyde	G		O
20	196	181, 196, 153	Acetosyringone	S	O	O
21		176, 204, 177, 161, 148	unknown		O	
22	210	167, 210, 123	Syringylacetone	S	O	O
23		146, 160, 189, 206, 104	unknown		O	O
24	194	194, 167, 139, 111, 177	Ferulic acid	G		O
25		190, 204, 162, 158, 147	unknown		O	O

G: guaiacyl-type lignin; S: syringyl-type lignin; O: Compounds detected

Table 5 Lignin contents and the number of phenolic hydroxyl groups over 100 C_9 units of lignin (PhOH/100C_9) determined by aminolysis method for the methanol-insoluble residues and untreated samples of oil palm and Japanese beech.

Sample	Methanol-insoluble residue			Untreated sample	
	Lignin (wt%)	Yield of lignin upon untreated sample (wt%)	PhOH/ 100C_9	Lignin (wt%)	PhOH/ 100C_9
Oil palm	99.2	10.3	36.5	29.6	28.4
Japanese beech	93.7	5.8	16.9	21.8	9.2

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Figure 1 Total-ion chromatograms for the methanol-soluble portion from oil palm and Japanese beech in GC-MS analysis.

Figure 2 Yields of the alkaline nitrobenzene oxidation products of the methanol-insoluble residues and untreated samples for oil palm and Japanese beech.

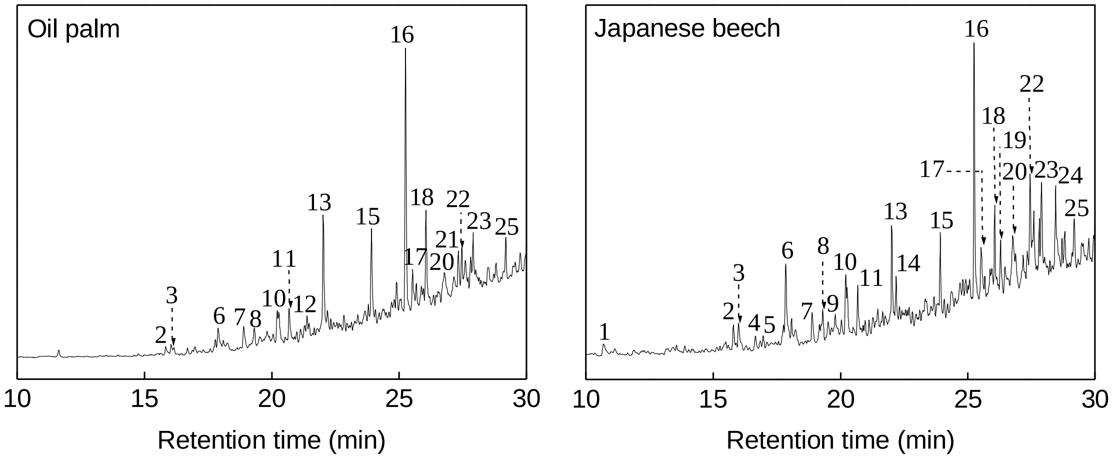

Figure 1 Total-ion chromatograms for the methanol-soluble portion from oil palm and Japanese beech in GC-MS analysis.

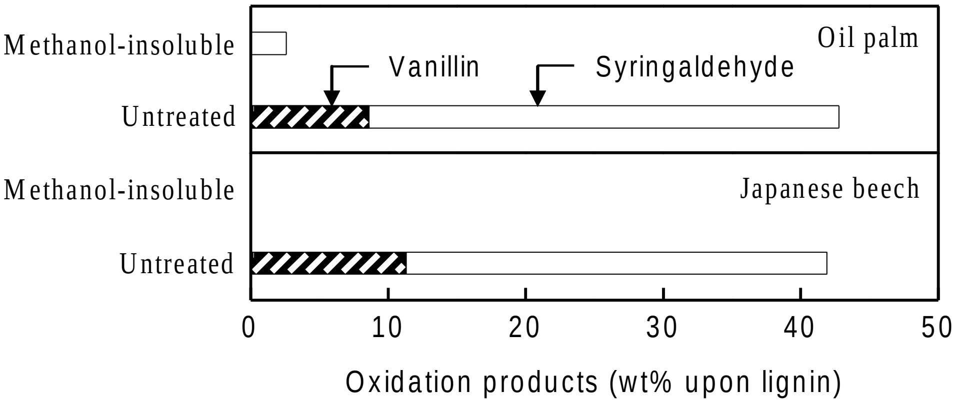

Figure 2 Yields of the alkaline nitrobenzene oxidation products of the methanol-insoluble residues and untreated samples for oil palm and Japanese beech.