Decomposition of lignin compounds from oil palm empty fruit bunch using ilmenite

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Abstract. Decomposition of lignin compounds into monomers from oil palm empty fruit bunches (OPEFB) has been successfully carried out. The purpose of this study was to determine the use of ilmenite as a lignin decomposer of OPEFB and to analyze the compounds produced using GC-MS method. The stages of the study consisted of preparation of ilmenite, pretreatment process of OPEFB, characterization of lignin isolates using FTIR, analysis of lignin content by UV-Vis, and photodegradation of lignin by GC-MS. Ilmenite was known to have a potential for decomposing the lignin compound through a photodegradation reaction, in the presence of ultraviolet light. The results of this study indicated that a time of five hours decomposition could have degraded lignin up to 50%. The longer the degradation time, the more lignin was degraded to produce materials in the form of phenolic compounds, furan compounds, benzene derivatives and carbon compound derivatives from lignin monomers. One of the benzene derivatives obtained was 3,4-di(methoxycarbonyl) benzoic acid (C₁₁H₁₀O₆).

1. Introduction

Palm oil production is currently increasing each year in Indonesia, with about 60 million tons of production per year[1,2]. The high production of oil palm may have produced wastes in the form of oil palm empty fruit bunches (OPEFB), which in turn would generate environmental hazard, if not utilized and handled properly[3–6]. Utilization and treatment of OPEFB waste has begun to be developed because it is known to have an important aromatic compound in the form of cellulose, hemicellulose and lignin. According to [7] lignin is an aromatic biopolymer of phenyl propane units with the second largest abundance after cellulose. Lignin with functional groups in the form of hydroxy, carbonyl and methoxy can be known for its composition using the photooxidation method, one of which is by using ilmenite, because it is known that phenolic derivatives and have high antifungal activity[8].

Ilmenite is a titanium-based compound that has the general form of FeTiO₃[9–12]. Ilmenite (FeO.TiO₂) is a modified material between TiO₂ and Fe dopants that can be synthesized using the sol-gel method using Titanium Tetra Isopropoxide compounds (Ti[OCH(CH₃)₂]₄)[13–15]. Utilization of TiO₂ compounds is currently very popular throughout the world because it has the ability of photocatalysts and is a very strong oxidizing agent when irradiated with ultraviolet (UV) light with a wavelength of 365-385 nm[16–19].

Ilmenite (FeO.TiO₂), a synthesis of TTIP, is used as a catalyst to decompose lignin which is expected to produce phenolic monomers such as coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol from lignin compounds[20,21]. Proof to find out that it has successfully decomposed lignin, it is necessary to measure the pure lignin absorbance as standardization and the lignin of decomposition results using UV-Vis. Meanwhile, to find out the monomers of lignin compounds, it is necessary to
conduct characterization tests using the Gas Chromatography Mass Spectrometry tool.

2. Experimental Methods

2.1. Making ilmenite (FeO.TiO$_2$)
The synthesis of ilmenite (FeTiO$_3$) was carried out using reflux method with controlled hydrolysis of TTIP with a mixture of acetyl aceton 0.5 mL and 15 mL ethanol 99%, with the composition of Solution 2 in the form of 15 mL 99% ethanol 99% and 2 mL distilled water by adding 1 mL acetic acid 0.1 M, stirring using a magnetic stirrer for 3 hours at 50 °C and adding Fe(NO$_3$)$_3$ to produce FeTiO$_3$ soles. The resulting sol was evaporated at room temperature for 48 hours to form a gel. The gel was then heated at 80 °C in the oven for 30 minutes, after which it was calcined at 500 °C for two hours, then the powered ilmenite was obtained and crushed using a mortal which was then characterized using XRD.

2.2. Sample preparation
Preparation until done by cleaning the OPEFB, then decomposed into a form of fiber and dried, reduced in size using a grinder up to 3-5 mm in size. The fiber was then ground using a grinding machine (blender) and sieved with a mesh filter of size 50. Then removes the OPEFB water content with the oven.

2.3. Pretreatment OPEFB
Pretreatment OPEFB was done by adding alkaline solution (NaOH) and acid solution (H$_2$SO$_4$). As much as 300 grams of OPEFB powder was added with a 10% NaOH solution of 1.5 L, then heated at a temperature of 150 °C. The pretreatment results were then filtered to produce solids and black liquor containing lignin [7].

The filtrate was then diluted by titration using 20% H$_2$SO$_4$ to pH 2 and heated at 60 °C, the sample was allowed to stand for 8 hours for complete precipitation. The lignin precipitate was separated from the black leachate using a centrifuge (4500 rpm, 20 minutes), then filtered to produce a lignin solution with higher purity. Subsequently the sludge was washed using 0.01 M H$_2$SO$_4$, washed with distilled water and filtered. The precipitate was dried in an oven (50-60°C) for 24 hours. After the sample preparation process, lignin was then analyzed using FT-IR and UV-Vis.

2.4. Photodegradation of Lignin
As much as 20 mL of isolated lignin solution was added with 0.1 gram ilmenite catalyst, inserted into the ultraviolet light reactor and stirred in each minute intervals, the solution was removed from the reactor filtered and absorbed using a UV-Vis spectrophotometer at maximum wavelength. The results of the photodegradation were continued characterization tests using Gas Chromatography-Mass Spectrometry (GC-MS).

3. Results and Discussion

3.1. Making Ilmenite (FeO.TiO$_2$) with the Sol-gel Method
The precursor in making ilmenite (FeTiO$_3$) was a TTIP compound with acetyl acetate used as a ligand to chelate titanium so that the yellow solution was also a stabilizer and inhibitor of hydrolysis of the TTIP compound when reacted with distilled water and ethanol. While ethanol functions as a hydrolysis rate controller because TTIP was very easy to transform into Ti(OH)$_4$ when it reacts directly with water. The mixture was then added to the compound Fe(NO$_3$)$_3$ as a source of Fe (II) to form the FeTiO$_3$ gel. Figure 1 a.

According to [22] the basic composition of FeTiO$_3$ production using the sol-gel method was (TTIP). These compounds in sol-gel the method acts as a medium or matrix distributor of dopant ions and forms nanoparticles, acetyl acetate as a chelating ligand which will produce an exothermic reaction and make a yellow solution. Making soles by adding FeTiO$_3$ can increase the photocatalysis activity acts as a trap of photoregeneration and electron holes so as to suppress the occurrence of electron-holes recombination[23,24]. The calcination process will obtain the FeTiO$_3$ composite powder shown in Figure 1 b.
3.2. Characterization of Crystal Size and Types of Ilmenite Crystals (FeTiO3) using XRD

X-Ray Diffractometer (XRD) was used to analyze the extracted ilmenite crystal phase so that specific peaks appear. Measurement using XRD aims to obtain information on the crystal structure of FeTiO3/Ti. XRD analysis was performed by comparing the 2 theta values with JCPDS (Joint Commite Powder Diffraction Standard) data. The XRD diffraction pattern of the synthesized ilmenite powder was adjusted to JCPDS anatase TiO2 crystal and ilmeniteanatase data. The diffractogram pattern was shown in Figure 2.

The XRD spectrum in Figure 2 shows that the synthase ilmenite has a peak of 25.2159; 33.0850; 37.0600; 37.7670; 47.9941; 49.1700; 53.8675; 55.8600; 62.5633; 68.7466; 70.1375; 74.8800. Anatase TiO2 was characterized by a peak at 2θ of 24.8; 37.3; 47.6; 53.5; 55.1 and 62.2 (JCPDS No. 21-1272). These results were in accordance with standard XRD data provided by JCPDS FeTiO3 No.24-4123 and JCPDS FeTiO3 No.29-0773. Ilmenite also shows that there were 6 peaks in the region of 2θ = 24 °, 32 °, 36 °, 40 °, 48 ° and 56 ° which were typical peaks of ilmenite crystals [25–27]. Based on XRD analysis, it is obtained the data of ilmenite compounds and crystalline forms that were compatible with the JCPDS database, so it can be used as a photocatalyst.

3.3. Identification of Lignin Function Groups with FT-IR Spectrophotometer

Fourier Transform Infra Red Spectroscopy (FT-IR) spectrometers were able to identify the typical uptake for each functional group contained in the lignin sample. Lignin compounds were generally identified by the appearance of several constituent groups such as absorption at wave numbers 3400-3450 cm⁻¹ for the -OH strain, 2820-2940 cm⁻¹ for the methyl -CH strain, 1600-1515 cm⁻¹ for the aromatic ring, 1460- 1470 cm⁻¹ for asymmetric strain -CH, 1330-1315 cm⁻¹ for stringile ring stretch, 1270-1280 cm⁻¹ for guasil ring, 1030-1085 cm⁻¹
for ether strain and 850-875 cm\(^{-1}\) for -CH aromatic. The results of the analysis of lignin isolates by FT-IR can be seen in Figure 3.

![FT-IR spectrum of Lignin isolate](image)

**Figure 3.** FT-IR spectrum of Lignin isolate

Based on the IR spectrum in the range of wave numbers between 500-4500 cm\(^{-1}\) and by comparing the groups of standard lignin compounds with the resulting lignin it can be seen that there were similarities with the general groups contained in lignin, so it can be concluded that the isolation results from the OPEFB compound were lignin compounds.

### 3.4. Decomposition of Lignin Isolates with UV Light and Ilmenite

The process of decomposition of compounds, carried out by photocatalysis was a combination of photochemical and catalyst. One of the compounds that can be used as a catalyst was ilmenite (FeO\(\cdot\)TiO\(_2\)). When the catalyst was exposed to UV light with energy greater than the band gap energy, it will produce a hole which was a strong oxidizing agent to form radicals OH that degrade lignin into simpler compounds[28,29]. Graph of Lignin Degradation Results Against Time Variations can be seen in Figure 4.

![Graph of Lignin Degradation Results Against Time Variation](image)

**Figure 4.** Graph of Lignin Degradation Results Against Time Variation

Based on Figure 4, it was known that the initial concentration of lignin 400 ppm with a variation of degradation time between 1 hour, 2 hours, 3 hours, 4 hours and 5 hours obtained the results of the percentage of degradation respectively 36.52%; 38.33%; 39.54%; 48.36% and 50%. These results indicate that the longer the degradation time, the more lignin was degraded in the compound. Increased degradation results due to lignin depolymerization, namely cleavage of ester bonds and ether bonds into simpler structures, but there can also be a reassociation reaction to rearrange condensed polymer structures to form new complexes [30–32].
3.5. Analysis of Lignin Decomposition Components with GC-MS

The results of lignin degradation were analyzed using GC-MS tools to determine the monomers of the lignin compound shown in Figure 5. The results of the GC-MS analysis showed that there were 35 monomer constituents of lignin that were degraded and there were 5 compounds that were successfully classified, these compounds can be seen in Table 1.

![Figure 5. GC chromatogram of degraded lignin samples](image)

| Retention Time (minute) | Area(%) | Compound Name |
|-------------------------|---------|---------------|
| 7.223                   | 2.96    | 3,4-di(methoxycarbonyl)benzoic acid |
| 9.774                   | 1.68    | 3-Methyl-2-(2-oxopropyl) furan |
| 13.743                  | 3.95    | 4-(3-ethoxy-2-methylpentyl)-2,6-dimethoxyphenol |
| 17.763                  | 4.54    | 4-(1-cyclohexylpropan-2-yl)-2-methylphenol |
| 18.289                  | 3.18    | Hexadecanoic Acid, Methyl Ester |

Based on the results obtained, the degradation of lignin monomers can be classified into four groups, namely phenolic (4-(3-ethoxy-2-methylpentyl)-2,6-dimethoxyphenol (C_{14}H_{21}O_{4}) derivatives); furan compound (3-Methyl-2-(2-oxopropyl) (C_{8}H_{10}O_{2})); Benzene derivatives (3,4-di (methoxycarbonyl)benzoic acid (C_{14}H_{10}O_{6})); and alkane derivatives (Hexadecanoic Acid (C_{17}H_{34}O_{2}) and 4-(1-cyclohexylpropan-2-yl)-2-methylphenol (C_{16}H_{30}O)).

4. Conclusion

The conclusion from the results of this study was the following Ilmenite compound which was synthesized using Titanium Tetra Isopropoxide (TTIP) can be used as a catalyst to degrade lignin from OPEFB. The results of decomposition through the photodegradation method were obtained in the form of phenolic compounds, furan compounds, benzene derivatives and carbon compounds.

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