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# Ultrasound-Assisted Extraction of Lignin from Oil Palm Frond

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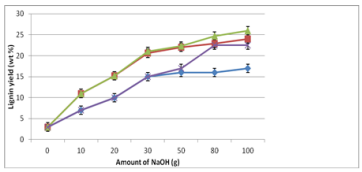
**Graphical abstract**




**Abstract**

Ultrasound-assisted method is claimed as a simpler and more effective ways of extracting compared to conventional extraction methods for the extraction of bioactive compounds from natural products such as lignin. This study investigated the potential of ultrasound-assisted extraction to extract lignin from oil palm frond (OPF) as compared to conventional heating. The extraction had been carried out by using sodium hydroxide solution as a solvent. Factors such as extraction temperature and solvent concentration were also examined. The presences of lignin in the corresponding extracts were confirmed by FTIR analysis. The result obtained showed that the extraction of OPF assisted with ultrasound was more efficient in giving higher lignin yield compared to conventional heating. Other than that, the reaction temperature was lowered down and the reaction time was also shortened when the extraction was assisted by ultrasound. With all these merits, ultrasound-assisted extractions were more effective to be used and should be considered for a wider application in the extraction of lignin and other compounds from various plants.

*Keywords*: Ultrasound-assisted method; oil palm frond; extraction; lignin production; sodium hydroxide



## 1.0 INTRODUCTION

The ecological, techno-economic and agro-climatic conditions were tending to be suitable for large scale planting of the oil palm in Malaysia. The industry grew rapidly and today, 4.69 million hectares of land in Malaysia is under oil palm cultivation and this contributes to about 37.3% of the world's total palm oil production. Malaysia is the leading producer and exporter of palm oil in the world and oil palm had been as one of the major driver for our country economic growth. At this time, the amount of biomass that had been left to rot and returned to the field as fertilizer is very vaunting. Malaysia has generated approximately 51 million tonnes of OPF, accounting for 53% of the total palm biomass in 2008 [1]. From this figure, it is expected that the ideas of extracting the lignin from OPF is very feasible to be explored.

Lignin represents 30% of all the non-fossil organic carbon and constituting from a quarter to a third of the dry mass of wood. Compared to other wood components (cellulose and hemicelluloses), it is a much more complex polymer and to use lignin as a material, the lignin must be removed from the wood [2]. The structure of lignin differs with the sources of wood, the process of dissolving the lignin from the wood and the isolation process. Lignin derived from OPF is expected to have potential features to substitute the expensive petroleum-derived phenolic compounds as a chemical feed stocks or fuels [3].

Nowadays, ultrasound-assisted extraction is evaluated as a simpler and more effective alternative to conventional extraction methods for the extraction of bioactive compounds from natural product. Ultrasonication is the application of high-intensity, high frequency sound waves (normally in the range of 20-100 kHz) to liquid or gaseous media. The propagation and interaction of sound waves alter the physical and chemical properties of materials that are subjected to ultrasonication due to its cavitation effect [4]. Cavitation induces localized high temperature and pressure and results in the production of highly reactive free radicals, such as $OH^-$, $H^+$, and $H_2O_2$, thus enhancing chemical reactions. The sonomechanical effect of ultrasound enhances the penetration of the solvent and heat into cellular material and thus improves the mass transfer. The use of ultrasound also results in disruption of biological cell walls to facilitate the release of cellular contents [5].

This work proposes a study on investigation of the effect of ultrasound applications during the process of lignin liquefaction. The use of ultrasound can enhance and increase the lignin yield. Moreover, it can shorten the process reaction time by inhibit the formation of large molecular structures during the liquefaction [6].

## 2.0 EXPERIMENTAL

### 2.1 Materials

Fresh oil palm frond (OPF) (less than a week after being cut down) and old oil palm frond (more than 2 month after being cut down) were collected from oil palm plantation. First, the OPF was washed and dried for 24 hour at 105°C. After that, the dried OPF were undergo further shredding and crushing in a high-speed rotary cutting mill and being sieve before sample with size 0.4-1 mm was chosen for extraction. Sulfuric acid ($H_2SO_4$) 96% and sodium hydroxide (NaOH) were analytical grade and purchased from commercial sources (QREC, New Zealand). The ultrasound-assisted extraction was carried out in an ultrasonic cleaning bath with an ultrasound power of 100 W, heating power of 400 W, and frequencies of 40 kHz. The device was equipped with timer and temperature controller.

### 2.2 Extraction of Lignin from OPF

The method used for the extraction was originally from a previous research [6] with some modifications by using ultrasound instead of microwave. The extractions were performed by mixing sodium hydroxide (NaOH) with 400mL of water as the cooking liquor and old OPF. The concentration of cooking liquor used was set as the manipulated variable for the experiment. The ratio of cooking liquor to the OPF in the mixture was 10:1. Then, the mixture was heated for 2 hours at a maximum temperature of 170°C carried out using an electrical mantel. The oil palm frond lignin was precipitated from the concentrated black liquor by acidified it to pH 2 using 20% sulfuric acid. The precipitate was filtered and washed with water of pH 2, which was prepared using the same acid as in the earlier step. The OPF lignin was then being filtered again and dried in an oven at 55°C for 24 hours prior to further analysis. The lignin obtained than was weighted and denoted as $W_P$.

These steps were then repeated by varying the amount of sodium hydroxide (0-100 g) to have a different solvent concentration. Besides that, the extractions were conducted using ultrasound-assisted method instead of the conventional heating. The temperatures of the ultrasonic bath were varied from room temperature to 80ºC by setting the temperature controller in the device. The amount of lignin yield was calculated using Equation 1,

$$\text{Lignin Yield \%} = W_P/W_F \times 100\% \quad (1)$$

where $W_P$ is the weight of lignin product (g) and WF is the weight of OPF feed (g).

### 2.3 Analysis of Lignin using FTIR

The FTIR spectrophotometer was performed using a Perkin Elmer System 2000 model. Each spectrum was recorded in a frequency range of 360-4000 $cm^{-1}$ at a resolution of 1 $cm^{-1}$ using KBr discs containing 1% finely ground sample. In addition, the sample spectrum was able to show the overall view of the lignin chemical structure [7].

## 3.0 RESULTS AND DISCUSSION

### 3.1 Effect of Sodium Hydroxide, OPF Source and Presence of Ultrasound on Lignin Yield

Figure 1 shows the weight percentage of lignin yield with the effect of NaOH, OPF source and presence of ultrasound. As can be seen, weight percentage of lignin extracted from old OPF was greater than from fresh OPF. Besides that, the amount of NaOH used as the solvent was also influence the amount of lignin yield. From the result, it also showed that the lignin yield was higher when ultrasonic was being used. It was reported that, when material in a liquid suspension are treated by ultrasonic energy, the particles are subjected to either surface erosion via cavitational collapse in the surrounding liquid or size reduction due to fission through interparticle collision or the collapse of cavitation bubbles formed on the surface [8]. Ultrasonic energy could crack the cell walls; dislocate the secondary wall of the middle layer and cause exposure and fibrillation [9]. Besides that, the propagation of ultrasound waves through liquids at frequencies ranging from 20khz to a few megahertz results in cavitation which causes various physical and chemical effects [10].

### 3.2 Effect of Temperature on Lignin Yield

Figure 2 shows the effect of temperature towards weight percentage of lignin yield. The experiment was conducted at constant NaOH at 100 g and using old OPF as the sample. As can be seen, the lignin yield was almost constant (about 13 %) at temperature ranged from 45 to 75°C. However, the lignin yield was increased dramatically from about 13 to 26% when the temperature was increased from 75 to 80°C. Reaction rates obviously will increase as the temperature increases since reaction rate is strongly dependent on the temperature. Furthermore, the molecules have more energy to distort their bonds to form another bond [11]. This observation is consistent with other study [12].

However, it was reported that if the reaction temperature is too high, the lignin yield started to decrease. Exceeding temperature at prolonged retention time could cause the presence of other components, due to decomposition of cellulose [13]. Lignin degradation could also occur when exposing lignin to the maximum operating temperature due to the cleavage of ether linkages in the lignin structures [11]. Besides, high temperatures usually lead to higher furfural (a carcinogenic compound) contents in the extract [14].

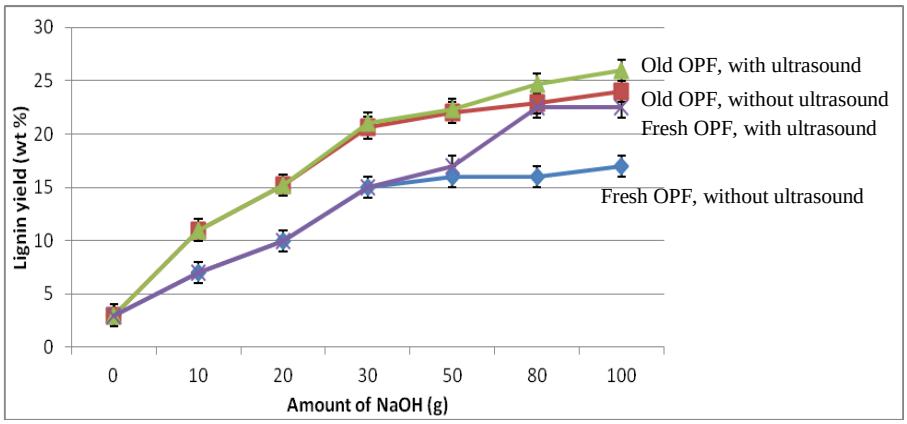



**Figure 1** Percentage of lignin yield with the effect of NaOH

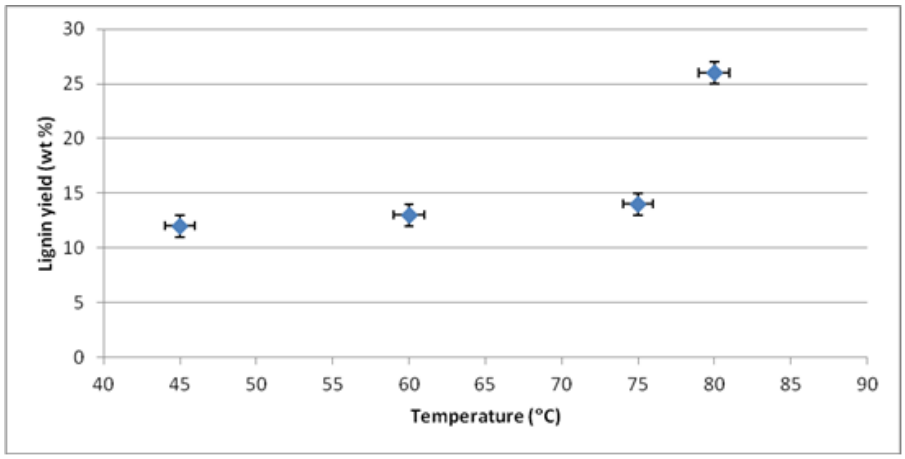



**Figure 2** Percentage of lignin yield with the effect of temperature

### 3.3 FTIR Analysis

FTIR analysis is frequently employed to represent the functional group compositional analysis of liquefied product from the liquefaction process. An infrared spectrum is unique to each substance and can hence, in principle, be used as an unbiased characteristic to identify a sample. The intensity of band depends on the magnitude of dipole change during the vibration. The larger change during the vibration will cause stronger absorption bands. As depicted in Figure 3, the broad band at 3423 $cm^{-1}$ was attributed to the phenolic and aliphatic OH group presence in the liquefied OPF. This strong band can be elucidated due to the structure of lignin, which is linked by carbon–carbon and ether bonds, including three major phenylpronanoid monomers, which are syringyl alcohol, guaiacyl alcohol and p-coumaric alcohol.

The three bands at 1646, 1509, and 1460 $cm^{-1}$ were attributed to aromatic ring vibration of the lignin skeleton. This value was approximately analogous to the bands reported from previous work [11]. The small bands at 1418 $cm^{-1}$ relates to C–H vibration of methyl group for the liquefied OPF. The small signal indicates that the conjugate C–H content in lignin of OPF were relatively low. The band at 1263 $cm^{-1}$ was due to the bending vibration of the syringyl ring breathing with C–O stretching. The guaiacyl ring was found at the bands 1221 $cm^{-1}$.The presence of syringyl and guaiacyl bands in the compounds indicated that liquefied product from liquefaction of OPF has a potential active site for polymerization process, precursor to resin formation [12].

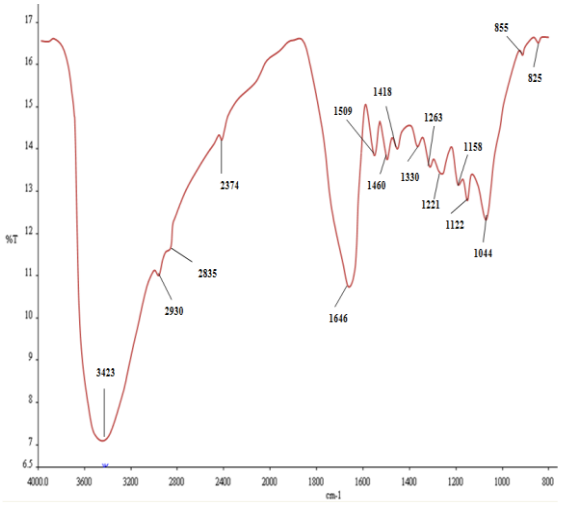



**Figure 3** FTIR spectra of lignin extracted from OPF

## 4.0 CONCLUSION

In this study, it could be concluded that the reaction parameters give significant effect on the yield of lignin extracted from the oil palm frond. The highest lignin yield of 26 % was achieved when

old OPF and ultrasound-assisted method was being used during the extraction. Besides that, the amount of sodium hydroxide used during the liquefaction also had a great influence on the yield. Other than that, reaction temperature also gave a momentous effect to the yield as higher temperature gave higher amount of the lignin yield.

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