



# Comparison of Oil Palm Empty Fruit Bunch Delignification at Room and Mild Temperature

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## ABSTRAK

Tandan Kosong Kelapa Sawit (TKKS) merupakan salah satu limbah berjenis padatan dari industri pengolahan minyak kelapa sawit yang dapat dimanfaatkan untuk bahan produksi pupuk, kertas, filler, dan komposit karena mengandung lignoselulosa yang tinggi yaitu sekitar 81-89%. Metode pemisahan lignoselulosa menjadi selulosa, lignin, dan hemiselulosa dilakukan dengan delignifikasi menggunakan  $H_2O_2$  dan penambahan katalis  $MnSO_4 \cdot H_2O$  yang dilakukan dengan dua percobaan yaitu dengan refluks pada suhu  $36^\circ C$  dan tanpa refluks pada suhu ruang ( $\pm 25^\circ C$ ). Rancangan percobaan dibuat menggunakan metode *Response Surface Methodology* (RSM) pada program Minitab 21. Tujuan dari penelitian ini adalah mengetahui kondisi optimum delignifikasi menggunakan katalis  $MnSO_4 \cdot H_2O$  untuk menurunkan kadar lignin dengan memvariasikan waktu serta komposisi katalis. Hasil penelitian menunjukkan kadar lignin terendah pada delignifikasi dengan dan tanpa refluks berturut-turut sebesar 19,71% (b/b) dan 18,24% (b/b). Kondisi optimum yang didapatkan dengan pengolahan RSM untuk delignifikasi refluks adalah pada waktu 6,83 jam dengan rasio katalis terhadap TKKS 11,03% (b/b). Sedangkan untuk delignifikasi tanpa refluks memiliki kondisi optimum pada waktu 3,38 hari dengan rasio katalis terhadap TKKS sebesar 3,76%(b/b).

**Kata kunci:** delignifikasi,  $H_2O_2$ , katalis, *Response Surface Methodology*, TKKS

## ABSTRACT

Oil palm empty fruit bunches (OPEFB) is one kind of palm oil industry solid waste. OPEFB contains high lignocellulose for about 81-89% that can be used for production of fertilizer, paper, filler, and composite. The separating method of lignocellulose into cellulose, lignin, and hemicellulose can be carried out by delignification using  $H_2O_2$  and  $MnSO_4 \cdot H_2O$  as catalyst. Two experimental designs were performed using the Minitab 21 program with *Response Surface Methodology* (RSM). Both designs have temperature as their dependent variable. The processes are carried out at  $36^\circ C$  and room temperature with the same variable independent, such as delignification time and concentration of the catalyst. The difference between these two designs is in their stirring process. Delignification that occurred at  $36^\circ C$  is processed under constant stirring, while delignification that occurred at room temperature is processed without stirring. This experiment aims to determine the optimum conditions for using Mn-catalyst in delignification by varying the time and catalyst concentration. The results show that the lowest lignin content in delignification with reflux is 19.71% (w/w), and for delignification without reflux is 18.24% (w/w). The optimum condition obtained by RSM for reflux delignification was at 6,83 hours with use of 11,03% (w/w) catalyst. Meanwhile, without reflux delignification, the optimum condition was at 3,38 days with a 3.76% (w/w) catalyst.

**Keywords:** delignification,  $H_2O_2$ , catalyst, *Response Surface Methodology*, OPEFB

## 1. INTRODUCTION

Oil palm empty fruit bunches are one of the solid wastes from the palm oil processing industry. Of each oil palm production, 23-30% are empty fruit bunches [1]. OPEFB is

often used as a fibre material because it has a high lignocellulose content. The chemical composition of OPEFB can be seen in Table 1. The components of cellulose microfibrils form spaces, the spaces between these microfibrils are filled with hemicellulose.



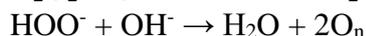
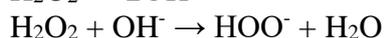
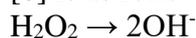
These spaces are tightly bound by lignin and form lignocellulose [3].

**Table 1.** Chemical composition of OPEFB [2]

No	Composition	Value (%)
1	Lignin	27,6 – 32,5
2	cellulose	41 – 46,5
3	Hemicellulose	25,3 - 33,8

Cellulose which is the main component of OPEFB lignocellulose is a polysaccharide with the general formula  $(C_6H_{10}O_5)_n$ , insoluble in water and some organic solvents such as benzene, ether, and others. Cellulose molecules have a linear shape which causes cellulose to be crystalline, strong, and not easily degraded [4]. Cellulose can be used for applications in various materials such as composite materials, paper, bioplastics, and foams [5]. The cellulose in lignocellulosic materials can be increased through a lignin separation process called delignification. In addition to reduce the lignin content, delignification can also reduce the crystallinity of cellulose, and increase the porosity of the material [1]. The delignification process can be carried out using  $H_2O_2$  because it does not damage the cellulose and lignin structure, and is free of chlorine so it is not harmful to the environment [6].  $H_2O_2$  in water will decompose into  $HOO^-$  and  $H^+$ . The  $HOO^-$  ion acts as a strong oxidizing agent.  $H_2O_2$  will oxidize aromatic compounds in lignocellulosic by releasing one electron and forming cation radicals which then decompose chemically. Most of these aromatic compounds are structurally found in lignin [7].

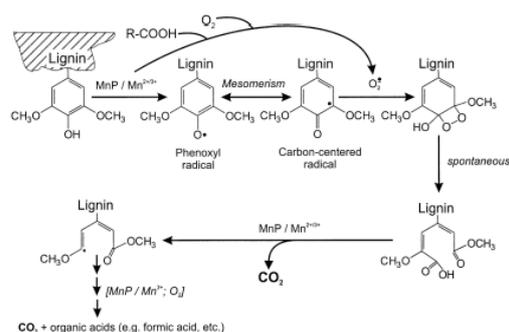
Reaction mechanism according to Jayanudin [8] is as follows:



$H_2O_2$  is an ideal oxidant in the delignification process, because it is safe for storage and handling, and produces by-products such as water and oxygen.  $H_2O_2$  requires an activator

for the reaction to run more rapidly. Mn catalyst is a heterogeneous catalyst that can be an activator for  $H_2O_2$  [9]. The use of Mn catalyst in delignification with  $H_2O_2$  obtained higher glucose yield compared to Fe catalyst [10]. The presence of Mn metal ions as a catalyst causes the lignin cleavage reaction to be faster than the delignification using only  $H_2O_2$ , because  $Mn^{2+}$  will be oxidized to  $Mn^{3+}$  which is more reactive caused reaction run more rapidly [11].

An illustration of the delignification mechanism using Mn is shown in Figure 1. The reduction of lignin begins after the phenol chain which is part of lignin structure is converted into a phenoxyl radical which loses  $H^+$  ions. Afterwards, it changes to its mesomer in the form of a carbon centered radical. Simultaneously oxidation occurs in the presence of  $O_2$  radicals to peroxy and other radicals which can release superoxide. The carbon-centered radicals then react to form unstable ether peroxides and result in chain cleavage and the formation of an aliphatic structure consisting of free carboxylic groups. Furthermore, the peroxide will separate the remaining chains and result in the formation of  $CO_2$ . The remaining aliphatic radicals undergo further reactions with dioxygen and formed more  $CO_2$  [12].



**Figure 1.** Illustration of Lignin Degradation [12].

## 2. RESEARCH METHOD

### 2.1 Preparation

#### 2.1.1 Experimental Design

The experimental design was carried out using Response Surface Method (RSM) and processed by Minitab 21 programme with 2

independent variables, namely time and amount of catalyst. The experimental design was carried out under two conditions, namely reflux at 36°C and without reflux at room temperature ( $\pm 25^\circ\text{C}$ ).

a. Experimental Design of Delignification at 36°C

The experimental design of delignification at 36°C is presented in Table 2. The selection of the lowest residence time (2 hours) was based on the optimum conditions of the study by Zuidar, et al. [6], meanwhile the highest residence time (6 hours) refers to the study of Ma, et al. [13].

**Table 2.** Parameter value Experimental Design of Delignification at 36°C

No	Independent variable	Lowest value	Highest value
1	time	2 hours	6 hours
2	catalyst composition	5% w/w	11% w/w

Data from Table 2 processed in Minitab 21 resulted an experimental design with a total run of 9 was obtained as shown in Table 3.

**Table 3.** Experimental Design of Delignification at 36°C

Run Order	Time (hour)	Catalyst ratio (%w/w)
1	2	5
2	6	5
3	2	10
4	6	10
5	1,2	7,5
6	6,8	7,5
7	4	3,96
8	4	11,04
9	4	7,5

b. Experimental Design of Delignification at room temperature

The experimental design delignification at room temperature is presented in Table 4. The selection of the residence time (4-7 days) refers to the study of Lucas, et al. [10].

**Table 4.** Parameter value Experimental Design of Delignification at room temperature

No	Independent variable	Lowest value	Highest value
1	time	4 days	7 days
2	Catalyst composition	5% w/w	11% w/w

Data from Table 4 processed in Minitab 21 resulted an experimental design with a total run of 9 was obtained as shown in Table 5.

**Table 5.** Experimental Design of Delignification at room temperature

Run Order	Time (days)	Catalyst ratio (%w/w)
1	4	5
2	7	5
3	4	11
4	7	11
5	3,38	8
6	7,62	8
7	5,5	3,76
8	5,5	12,24
9	5,5	8

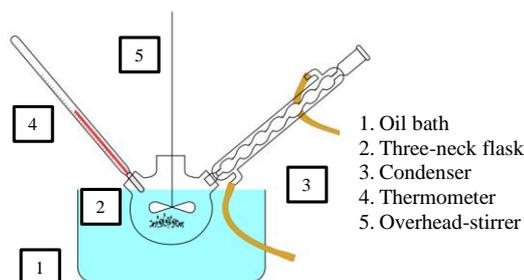
### 2.1.2 Pre-treatment

OPEFB was washed using distilled water and then dried in an oven at 105°C for 3 hours. After that, the dried OPEFB were then grinding and sizing using a grinder and sieve shaker until the size became 120-230 mesh (63-125 microns).

## 2.2 Delignification

Delignification was carried out by putting 5 grams of OPEFB, 150 ml of 30%  $\text{H}_2\text{O}_2$  and a catalyst of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  with various

concentrations according to the experimental design into a three-neck flask with reflux and into a beaker for a delignification without reflux (Figure 2). During the process, stirring was carried out for the delignification with reflux and not stirred for the delignification without reflux. The series of equipment in the delignification process at 36°C is shown in the following figure:



**Figure 2.** Delignification apparatus at 36°C

A sample obtaining from the delignification process was neutralized by rinsing the sample with distilled water. The neutralized sample was then dried using an oven at 105°C for 2 hours.

## 2.3 National Renewable Energy Laboratory (NREL) Analysis

### 2.3.1 Sample preparation

Preparation of the sample begins by inserting 0.3 grams of dry OPEFB dry sample and 3 ml of 72%  $H_2SO_4$  solution into an erlenmeyer then stir briefly. After that, erlenmeyer was stored in an incubator shaker at a temperature of 30°C with a rotation set of 120 RPM for 60 minutes. After shaking, 84 ml of distilled water was added to the sample solution and the sample solution was sterilized in an autoclave at 121°C for 15 minutes. After completion, the solution is cooled and then filtered by a vacuum pump. After being separated, the liquid phase was stored and separated (filtrate) from the solid phase (residue).

### 2.3.2 Lignin Analysis

Analysis of lignin content is divided into two types, namely acid soluble lignin, and acid insoluble lignin. Acid-soluble lignin analysis was carried out using a UV-Vis spectrophotometer at a wavelength of 250 nm (the sample was the liquid phase). Furthermore, for the analysis of acid insoluble lignin was carried out gravimetrically for the solid phase. Samples were dried using an oven at a temperature of 105°C for 5 hours and then furnace in a furnace at a temperature of 575°C for 4 hours.

## 3. RESULTS AND DISCUSSION

### 3.1 Delignification

OPEFB delignification is carried out to reduce lignin content. The solvent used in this delignification is  $H_2O_2$ , which is clear solution turn dark brown after adding OPEFB and catalyst into it.



(a)



(b)



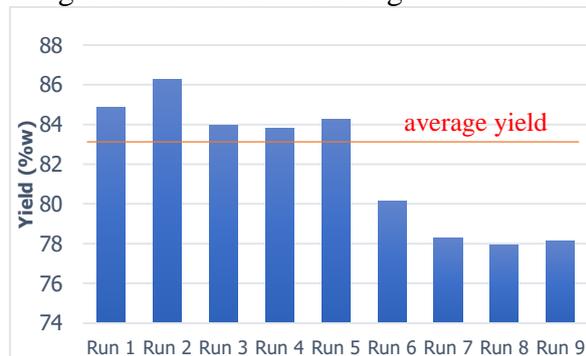
(c)

**Figure 3.** (a) raw OPEFB, (b) delignified OPEFB (delignification at 36°C), (c) delignified OPEFB (delignification at room temperature).

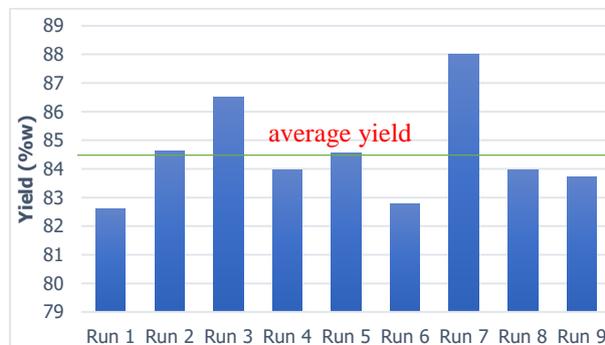
After a while, a foam formed at the top of the solution. This delignification process ultimately produces a brown solution with a light brown residue. This is because the  $H_2O_2$  solution is a bleaching agent. Delignified OPEFB is shown in Figure 3

### 3.2 Yield of Delignification

The yield of delignification in each experimental variation indicate that there has been a separation between cellulose with lignin and hemicellulose. The yield of delignification is shown in Figure 4 and 5.



**Figure 4.** Yield of delignification at 36°C



**Figure 5.** Yield of delignification at room temperature

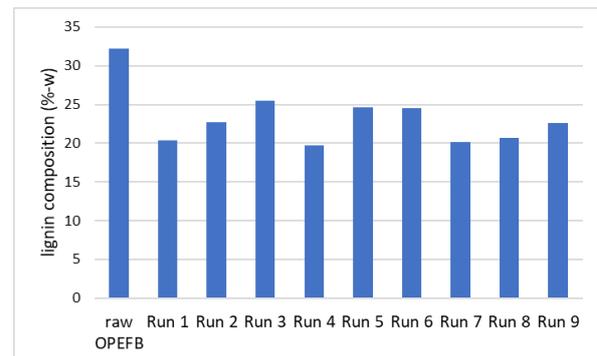
Figure 4 shows the yield of delignification process at 36°C is still relative high, ranging from 78 – 86%-w with the lowest yield in run 8, which is 77.95%-w and the largest yield in run 2, which is 86.27%-w. Figure 5 shows the yield of delignification process at room temperature between 82 – 88%-w with the lowest yield found in run 1, which is 82.59%-w and the largest yield is found in run 7, which is 88.02%-w.

The weight decrement in the material or sample occurs because the delignification reduces lignin and hemicellulose which increases the purity of the cellulose. Cellulose remains in the solid phase whereas hemicellulose and lignin are dissolved in  $H_2O_2$  and  $MnSO_4 \cdot H_2O$  solutions. Therefore, weight reduction related to separation of hemicellulose and lignin.

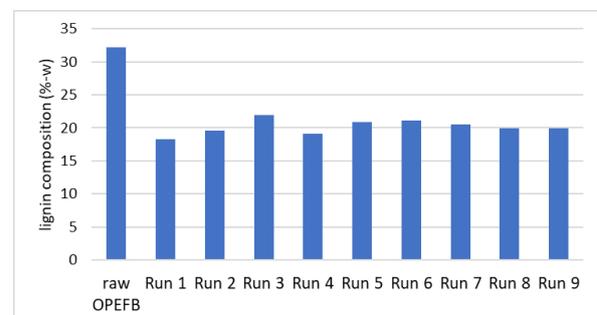
The hemicellulose is reduced because  $H_2O_2$  in acidic conditions can break glycoside bonds because the glycoside bonds in hemicellulose are very sensitive to acid and have a lower degree of polymerization compared to cellulose which causes dissolution of hemicellulose [7].

### 3.3 Analysis of Lignin Content

The results of the analysis of the lignin composition are shown in Figure 6 and Figure 7.



**Figure 6.** Lignin Composition from delignification at 36°C

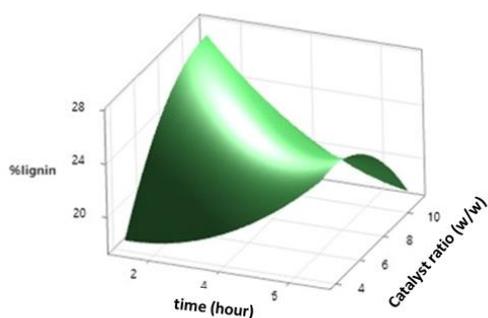


**Figure 7.** Lignin Composition from delignification at room temperature

Figures 6 and 7 show that in the experiment at 36°C, the lignin composition in the delignified OPEFB ranged from 19.71 to 25.46%-w, while in the experiment at room temperature, the lignin composition in the delignified OPEFB varies from 18.24 to 21.95%-w. The decrease in lignin reaches 13% compared to the initial lignin composition of OPEFB which was 32.21%-w. The decrease in lignin occurs due to bond breaking through delignification, namely oxidizing the hydroxyl group to a carbonyl group, followed by a glycosidic bond breaking reaction in an acidic environment [6].

The decreasing of lignin composition delignification at room temperature result in the lowest lignin composition (18.24%-w). Meanwhile, in the delignification at 36°C, the largest decrement in lignin result in a total lignin content of 19.71%-w.

The relationship between the ratio of catalyst and time to lignin composition in delignification at 36°C can also be seen in Figure 8. Lower lignin composition can be shown at times lower than 6 hours and catalyst ratios greater than 11% w/w.



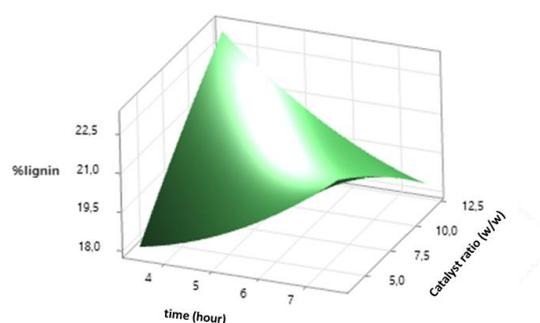
**Figure 8.** Delignification at 36°C contour plot

The relationship between the ratio of catalyst and time to lignin composition in delignification at room temperature is illustrated by the contour plot in Figure 9. The figure shows that the smallest lignin content can be achieved in less than 4 days with a catalyst ratio of less than 5% w/w.

These results are inversely proportional to the theory which states that the longer the delignification time, the lower the lignin content of the product. This can happen because the reaction finish completely, so that there is no more  $\text{H}_2\text{O}_2$  donating electrons or no more  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  that performs redox reactions.

The reaction mechanism is estimated as illustrated by Hofrichter [12] in which the metal ion Manganese ( $\text{Mn}^{2+}$ ) is oxidized by oxygen air to  $\text{Mn}^{3+}$  ion. Then  $\text{Mn}^{3+}$  metal ions and  $\text{H}_2\text{O}_2$  compounds oxidized lignin compounds. The lignin compound will form its radicals so that the compound is unstable and there is deliverance of lignin from lignocellulosic OPEFB which called delignification.

Lignin radicals will reduce metal ions  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  again. However, it is estimated that the redox cycle of the metal ion  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and vice versa cannot occur continuously. This causes extending the reaction time does not decrease the lignin content as shown in Figures 8 and 9. However, the amount of catalyst plays a very important role in reducing lignin levels where the more Manganese catalyst, the more lignin compounds are degraded.



**Figure 9.** Delignification at room temperature contour plot

In addition, other things that might happen according to Rembet [14], at higher temperature conditions and higher catalyst can cause an increase lignin composition. The longer the delignification reaction, the more new monomers formed due to the

breakdown of lignin. The monomer will react with the polymer that is still contained in the material and produce a new polymer/lignin which is difficult to separate.

### 3.3 Determination of Optimum Conditions for lowering Lignin Composition

Determination of the optimum conditions by RSM in the delignification at 36°C is shown in Table 6 and the delignification at room temperature is shown in Table 7.

**Table 6.** Optimum Condition of delignification at at 36°C

optimum time (hour)	Catalyst ratio (w/w)	Lignin composition (%-w)
6,8	11,03	17,82

**Table 7.** Optimum Condition of delignification at room temperature

optimum time (day)	Catalyst ratio (w/w)	Lignin composition (%-w)
3,38	3,76	18,05

The lignin composition of the optimized delignified OPEFB is still high. This indicates that there is optimum condition that exceeds the range of variation in the experiment.

### 8.4 Effect of MnSO<sub>4</sub>.H<sub>2</sub>O Catalyst on Delignification

The delignification was carried out without using MnSO<sub>4</sub>.H<sub>2</sub>O catalyst at 36°C and room temperature. Table 8 show a comparison of the lignin composition of the delignified product at optimum conditions with and without MnSO<sub>4</sub>.H<sub>2</sub>O catalyst. Table 8 shows that delignification not only influenced by H<sub>2</sub>O<sub>2</sub> but also MnSO<sub>4</sub>.H<sub>2</sub>O catalyst.

**Table 8.** Effect of catalyst on delignification at 36°C and room temperature at optimum conditions

Delignification condition	Lignin Composition (%-w)		
	Raw OPEFB	Without catalyist	With catalyst MnSO <sub>4</sub> .H <sub>2</sub> O
at 36°C		24,04	19,71
		32,21	
room temperature		20,68	18,24

## 4. CONCLUSION

Delignification at mild condition which held at 36°C and room temperature can reduce lignin composition of OPEFB which is not only influenced by H<sub>2</sub>O<sub>2</sub> but also MnSO<sub>4</sub>.H<sub>2</sub>O catalyst. The lowest lignin composition (19.71%-w) of delignified OPEFB is found in the operation condition of 6 hour delignification and the catalyst ratio of 10% w/w, which delignification at 36°C experiment. Meanwhile, delignification at room temperature, the lowest lignin composition (18.24%-w) of delignified OPEFB is found in the operation condition of 4 days and the catalyst ratio of 5% w/w. Further study about condition operation of delignification at mild condition should be conducted due to the economy of the process.

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