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PRETREATMENT OF EMPTY PALM FRUIT BUNCH FOR LIGNIN DEGRADATION

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Abstract. The potential of three chemical pretreatment methods for lignin degradation of empty palm fruit bunch (EPFB) was investigated. In method 1, sodium hydroxide (NaOH) and calcium hydroxide ($Ca(OH)_2$) bases were exclusively used as degradation agents. In the second method, hydrogen peroxide (H_2O_2) was simultaneously added with the base while the third method H_2O_2 was consecutively added into the EPFB-base mixtures after 24 h. The percentage of ligin degradation were 65%, 72% and 99% by using NAOH and 9%, 31% and 44% by using ($Ca(OH)_2$) for methods 1, 2 and 3 respectively. For the same conditions, NaOH demonstrated better performance than $Ca(OH)_2$ and method 3 was the most superior.

Keywords: Lignocellulose degradation; phenol; empty palm fruit bunch; chemical pretreatment

Abstrak. Potensi bagi tiga kaedah prarawatan kimia terhadap degradasi lignin tandan kelapa sawit kosong (EPFB) telah dikaji. Pada kaedah pertama, natrium hidroksida (NaOH) dan kalsium hidroksida $(Ca(OH)_2$ digunakan secara keseluruhan sebagai agen degradasi. Pada kaedah kedua, hidrogen peroksida (H_2O_2) ditambah serentak bersama alkali manakala untuk kaedah ketiga H_2O_2 ditambah berturutan ke dalam campuran EPFB-alkali selepas 24 jam. Peratus degradasi lignin adalah 65%, 72% dan 99% menggunakan NaOH manakala 9%, 31% dan 44% menggunakan $(Ca(OH)_2$ bagi kaedah 1, 2 dan 3 masing-masing. Dalam keadaan yang sama, NaOH menunjukkan potensi yang lebih baik berbanding $(Ca(OH)_2$ dan kaedah ketiga adalah merupakan kaedah yang terbaik.

Kata kunci: Degradasi lignoselulosa; fenol; tandan kelapa sawit; prarawatan kimia

1.0 INTRODUCTION

Generally biomass consists of three major components: cellulose, hemicellulose, and lignin. Recently, lignocellulose was reported to be the most favored and valuable compound in biofuel production [1]. The structures of lignin [2], cellulose [3] and hemicellulose [3] are shown in Figures 1 – 3.

Lignocellulose can be converted into important chemicals via pyrolysis technology. Flash pyrolysis of lignocellulose produces a wide variety of low molecular weight products, typically rich in alkenes. Phenolic compounds, alkanes, and aldehydes were also produced as the major products depending on the pyrolysis conditions [4].

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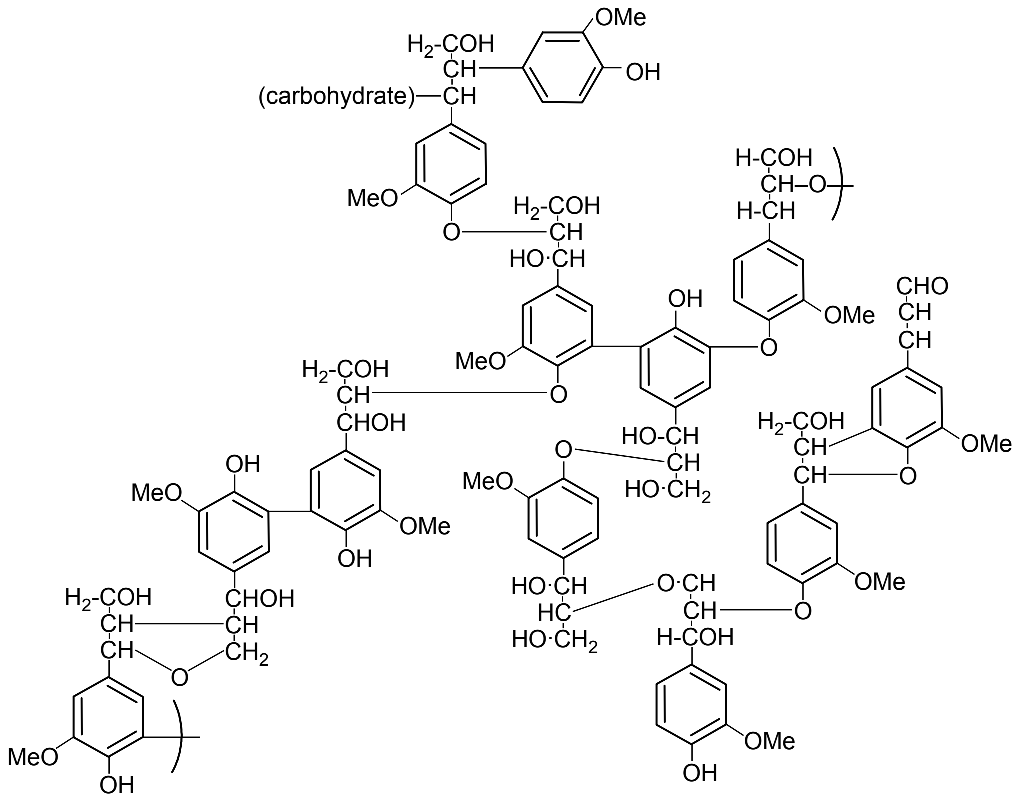

Figure 1 Structure of lignin compounds in biomass [2]

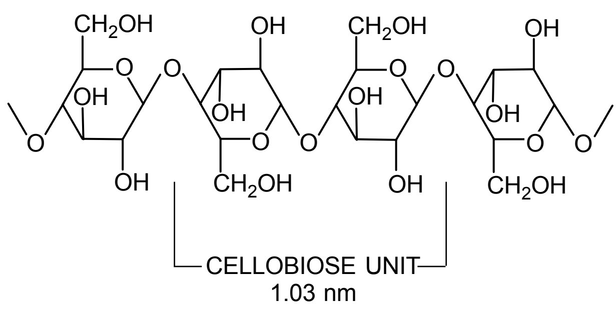

Figure 2 Schematic illustration of the cellulose chain [3]

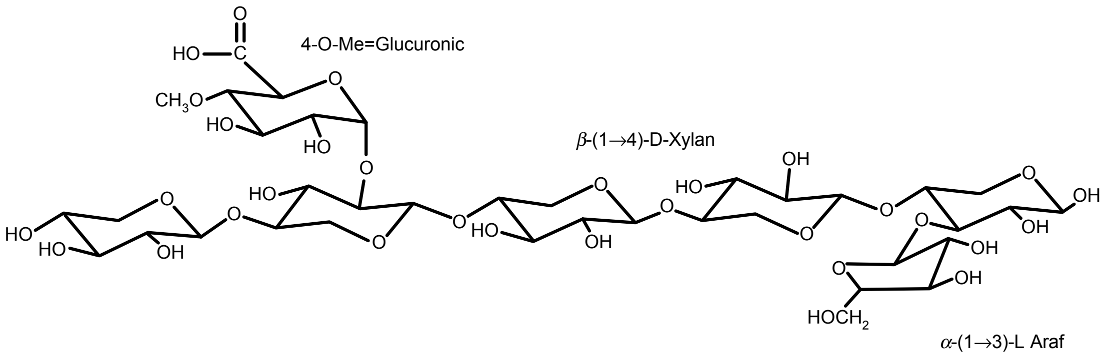

Figure 3 Schematic illustration of the cellulose chain [3]

Among the three compounds in biomass, lignin is the most complex structure with high molecular weight and insolubile. Thus, lignin is hardly degraded at typical biomass pyrolysis temperature of 300 to 500°C [5 – 7]. One of the most promising alternatives is for the raw materials to be pretreated before thermo-chemical conversion or pyrolysis takes place.

In recent years, there have been many studies on pretreatment of lignocellulosic biomass materials either chemically or physically [8]. The pretreatment has been widely reported for the purpose of alteration of lignocellulosic materials for pulp Kraft industries, lactic acid and bioethanol production [9]. In another study, pretreatment was employed to alter or remove structural and compositional impediments to hydrolysis to improve the rate of enzyme hydrolysis and increase yields of fermentable sugars from cellulose or hemicellulose [10].

Chemical pretreatment has been widely reported as a potential technique for lignocellulose degradation. The techniques include using acid and alkaline pretreatments, liquid hot water, pH controlled hot water and flow-through liquid hot water [8]. The alkaline pretreatment was however favored since lower temperatures and pressures could be employed compared to other pretreatment technologies. It may be carried out at ambient conditions and is generally more effective on agricultural residues and herbaceous crops [10]. The potential of sodium hydroxide (NaOH) and hydrogen peroxidase (H_2O_2) in treating cotton stalks has been reported [10]. Another chemical that is commonly used is calcium hydroxide. The chemical is a low reagent cost and can be recovered from water as insoluble calcium carbonate by reaction with carbon dioxide. The carbonate can then be converted to lime using established lime kiln technology [11].

The pyrolysis technology for biomass conversion is generally a thermal degradation process in the absence of an externally oxiding agent. Typical pyrolysis is conducted under moderate temperature and short residence time in the presence of catalyst. Generally, pyrolysis products consist of bio-oil (condensable gas), synthetic gas (noncondensable gas), and char [6]. Modern catalytic cracking uses zeolite catalysts which have shown excellent performance as solid acid cracking catalysts due to higher selectivity [12 – 13].

The easiest and cheapest lignocellulose resources can be found in oil palm biomass [14]. Fibrous derivatives from palm oil industry's solid waste, especially the oil palm fiber from empty fruit bunch (EFB), present a renewable source of non-wood lignocellulosic materials. Lignocellulosics have attracted significant research attention as they represent a major obstacle in chemical pulping, forage digestibility, and processing of plant biomass to biofuels. Since lignocellulosics contain valuable compounds for chemicals rich in hydrocarbons, the pre-treatment method is useful to degrade the lignocellulose. Ibrahim *et al.* [14] has reported that soda lignin may be extracted from black liquor of oil palm empty fruit bunch (EFB) fibers using 20% (v/v) sulfuric acid.

The objective of this study is to investigate different chemical methods in degrading EPFB lignocellulose structure. The degree of the degradation is monitored based on the amount of lignin. The chemical methods could degrade the lignocellulosic structures and disassemble the chains besides increasing the accessible surface area of of EPFB to produce important chemicals during pyrolysis. The concept of the pretreatment process is illustrated in Figure 4.

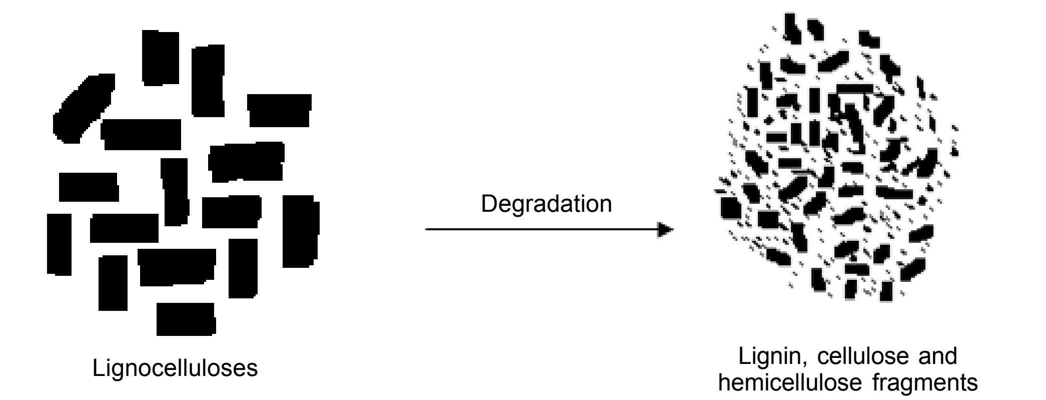

Figure 4 Pretreatment concept of lignocellulosic material

2.0 EXPERIMENTAL

2.1 Biomass

Seasoned EPFB sample aged approximately 6 – 12 months was obtained from Felda Taib Andak, Kulai, Johor. It was crushed and grinded in a high-speed rotary cutting mill to give particle size ranging from 0.5 – 1.0 mm. The sample was dried at 105°C for 24 h prior to the experiments. The properties of the raw material, proximate and elemental analysis are given in Table 1 [15].

Table 1 Main characteristics of EPFB (wt%) [15]

Proximate analysis (%)	
Cellulose	59.7
Hemicellulose	22.1
Lignin	18.1
Ash	5.36
Elemental analysis	
Carbon	47.89
Hydrogen	6.05
Nitrogen	0.65
Oxygen	45.41
Empirical formula	$H_{1.51}N_{0.01}O_{0.95}$
H/C molar ratio	0.1263
O/C molar ratio	0.9482
N/C molar ratio	0.0136
High heating value (MJ/kg)	16.7405

2.2 Pretreatment Condition

Three chemical pretreatment methods were employed in this study. Two bases, 50 mL sodium hydroxide (NaOH) and 50 mL calcium hydroxide ($Ca(OH)_2$) at 100 mM concentration were used to pretreat 5 g of the EPFB samples in each method. Under constant stirring and temperature at 90 rpm and 27°C respectively, the samples were treated in a 250 mL Erlenmeyer flask for 48 h. The description of the three different methods is tabulated in Table 2.

The first method was conducted over a single type of base, either using NaOH or $Ca(OH)_2$ whilst in the second method, hydrogen peroxide (H_2O_2) and the bases were added simultaneously to EPFB/NaOH + H_2O_2 and EPFB/$Ca(OH)_2$ + H_2O_2

Table 2 The effect of pretreatment methods on Kappa Number and lignin degradation

	Independent variables		**Dependent variables**		
Run	**Chemical pretreatment method**	**Chemicals**	**Kappa Number, *K***	**Lignin Content (wt%)**	**Lignin Degradation (%)**
1	Untreated		48.29	7.24	0
2	Method 1	$Ca(OH)_2$	43.75	6.56	9
	(single chemical)	NaOH	17.05	2.56	65
3	Method 2	$Ca(OH)_2 + H_2O_2$	33.39	5.01	31
	(H_2O_2: added simultaneously)	$NaOH + H_2O_2$	13.71	2.06	72
4	Method 3	$Ca(OH)_2$–H_2O_2	27.12	4.07	44
	(H_2O_2: added consecutively)	NaOH–H_2O_2	0.68	0.10	99

mixtures respectively. In the last method, H_2O_2 was added consecutively after a 24 h EPFB pretreatment with either base and treated for another 24h. At the end of the reaction, the pretreated EPFB samples were filtered, washed dried overnight in the oven at temperature 100°C.

The duration of all experiments were kept constant for 48 h of pretreatment period for all the three methods. A total of seven experiments were performed to investigate the effects of chemical pretreatment method on lignin degradation. Control experiment without chemicals was carried out under constant stirring and temperature at 90 rpm and 27°C for 48 h. All the experiments were repeated for three times in order to confirm the repeatability of the results.

2.3 Lignin Content Determination

An amount of pretreated and untreated EPFB (0.1 g) was added into a mixture of 20 mL of 0.02 mol/L potassium permanganate ($KMnO_4$) and 5 mL of 2.0 mol/L sulfuric acid (H_2SO_4), and shaked well for three minutes. The solid sample was separated from the solution through filtration, while the filtrate was measured using UV-Spectrophotometer (Shimadzu, USA) at 546 nm of wavelength. The One-Point calibration method was carried out to determine the value of Kappa Number, K [16], which is shown in Equation (1).

$$K = \frac{a}{w}\left(\frac{A_o - A_e}{A_o}\right) \tag{1}$$

where K is Kappa Number, a is the volume of $KMnO_4$ used in the solution, w is weight of moisture-free sample used, A_o is spectral intensities at time t = 0 (before sample is being added) and A_e is spectral intensities at the end of the reaction.

Accordingly, lignin content in the sample was calculated from the values of Kappa Number, K using Equation (2) [16]:

$$Lignin\,(wt\%) = 0.15K \tag{2}$$

3.0 RESULTS AND DISCUSSION

Direct spectroscopic Kappa Number determination was employed in this study to determine the lignin content in samples (Table 2). In general, Kappa Number is proportional to the lignin content [17]. Lignins are aromatic polymers that are present mainly in secondarily thickened plant cell walls [1]. Lignin is the most difficult component to be degraded due to its complex structure, high molecular weight and high insolubility.

Through the pretreatment process applied, it was observed that a significant reduction in lignin content has been achieved as compared to the original untreated

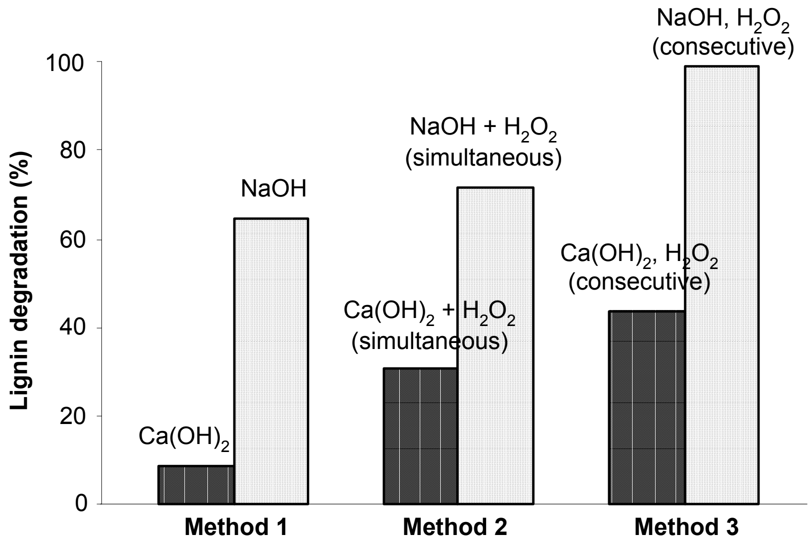

Figure 5 Effects of chemical pretreatment methods on lignin degradation for 48 h of pretreatment period

substrate. All three methods demonstrated different capacity in lignin degradation. The performance may be best described by the percentage of delignification as illustrated in the histograms in Figure 5. The percentage is calculated by dividing the difference between lignin content of untreated and treated EPFB samples to the lignin content in the original untreated EPFB.

According to the results, similar trend of lignin degradation performance was observed. The results demonstrated that the use of NaOH chemical gave encouraging performance in all the three methods conducted. Roughly, there was approximately 50% difference of lignin degradation capacity between NaOH and $Ca(OH)_2$ in all methods executed. For instance, in the first method, NaOH managed to give 65% of lignin break down which is 7.2 times higher than $Ca(OH)_2$ (9%). Theoretically, NaOH is able to degrade lignin by breaking the ester bonds cross-linking lignin. As a result, it facilitates in increasing the porosity of biomass [10].

The impact of degradation seems to be more significant when another chemical was added in the reaction. The introduction of H_2O_2 as a co-chemical agent in the second method has shown a remarkable improvement in lignin breakdowns for both chemicals. The activities of H_2O_2 enhance enzymatic conversion through oxidative delignification and reduction of cellulose crystallinity [18]. The purpose of H_2O_2 addition is to detach and loosen the lignocellulosic matrix [19].

According to Figure 5, the combination of NaOH-H_2O_2 in Method 2 managed to increase the degradation capacity from 65 % in the first method to 72%. Meanwhile, the impact of $Ca(OH)_2$-H_2O_2 demonstrated a noteworthy improvement in the degradation from 9% to 31%. It was observed that the combination of $Ca(OH)_2$-

H_2O_2 gave greater impact on degradation improvement (3.4 times) compared to NaOH-H_2O_2 (1.1 times).

As reveal in Figure 5, method 3 displayed the greatest ability in lignin removal regardless of the chemicals used in all the methods. Most interestingly, complete lignin removal was successfully achieved when NaOH and H_2O_2 were used consecutively in the pretreatment. Their synergistic activities combine the function of NaOH in hydrolyzing chlorolignin and H_2O_2 in oxidizing the lignin structure. According to Rebecca *et al.* [10], an increase of NaOH concentration significantly improved lignin degradation capacity when temperature and residence time are combined. Lime ($CaCOH_2$) has been used to pre-treat wheat straw at 85°C for 3 h [19], poplar wood at 150°C for 6 h with 14-atm oxygen [20], and corn stover at 100°C for 13 h [21].

When $Ca(OH)_2$ and H_2O_2 were used consecutively in this technique, a lower delignification performance which is just about 44 % is reported. This may be due to

Table 3 Reported studies of chemical pretreatment on the delignification of biomass

Author	Chemical	Biomass	Process Condition	Lignin Degradation (%)	Application
This study (Method 3)	**NaOH-H_2O_2**	**EPFB**	**Temp: 27°C Time: 48 h**	**99**	**Biofuel Production**
	$Ca(OH)_2$-H_2O_2	**EPFB**	**Temp: 27°C Time: 48 h**	**44**	**Biofuel Production**
Chang *et al.* [23]	$Ca(OH)_2$	Wood chips	Temp: 150°C Time: 6 h	78	Glucose Production
Playne, [19]	$Ca(OH)_2$	Sugarcane bagasse	Ambient conditions, 192 h	72	–
Rebecca *et al.* [10]	H_2SO_4	Cotton stalk	121°C, 90 min, 2%	24	Ethanol Production
	NaOH		121°C, 90min, 2%	66	
	H_2O_2		121°C, 60 min, 2%	30	
Ohgren *et al.* [24])	Steam pretreatment (impregnated with SO_2)	Corn stover	190°C, 5min, 3%	48	Sugar production (hexoses and pentoses)
			170°C, 9 min, 3%	42	
Xu *et al.* [9]	Ammonia liquor	Soybean straw	10%, 24h, room temperature	30	Lactic acid

the alkalinity strength of $Ca(OH_2)$ which is lower than NaOH. Rebecca *et al.*, [10] has reported that H_2O_2 pretreatment only contributed to 6.22% delignification at 0.5% concentration for 90 min reactions at 90°C temperature. Another study has reported that H_2O_2 managed to degrade lignin of sugar cane bagasse for barely 50% [22].

In general, alkaline pretreatment has been widely established for the purpose of alteration of biomass materials for pulp Kraft industries, lactic acid and bioethanol production [9, 10, 22]. In this study, the technique was manipulated to alter the lignocellulosic structure of EPFB for the intention to produce chemicals. The pretreatment is primarily employed to degrade the lignin structure. The superiority of the pretreatment seems comparable to other pretreatment methods as reported in other studies tabulated in Table 3. The use of NaOH for treating cotton stalk at 121°C was observed to give barely 66% of lignin degradation [10]. An almost complete lignin degradation of EPFB was reported in this study. Interestingly, the pretreatment was carried out under low temperature of 27°C. The low temperature signifies reduced energy consumption for the process.

4.0 CONCLUSIONS

Pretreatment of EPFB by using NaOH and H_2O_2 has proven to be the best method in lignin degradation as 99% of the lignocellulosics were degraded compared to other methods and studies. Higher degradation, shorter preparation period and lower temperature condition seem to make the pretreatment method attractive for EPFB application to biofuel and biochemical industries.

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