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DELIGNIFICATION OF OIL PALM EMPTY FRUIT BUNCH UNDER MILD CONDITIONS BY AIR OXYGEN AND MANGANESE GLUCONATE

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The oil palm empty fruit bunch (OPEFB) as a lignocellulosic material is available abundantly in Indonesia, because this country is one of the world's largest producer of crude palm oil. Pre-treatment of lignocellulosic biomass is a necessary step to break the lignin and hemicellulose structure and makes polysaccharides easily available for enzyme digestion. The aim of this study was to evaluate the performance of lignocellulose pre-treatment with air oxygen catalysed by manganese gluconate complex at temperatures below 343 K and pH of 8–9.5. Delignification experiments were carried out in a reactor flask which equipped with a heater, stirrer, reflux condenser, thermometer, and air injection channel. The optimum delignification results based on kappa number values were around 93 at pH of 8.5 for 4 hours, and temperature of 338 K, mass ratio Mn^{2+} to OPEFB (%) of 0.33, volume soaking solution of 125 ml, molar ratio gluconic acid/Mn^{2+} of 15:1 and air flow rate of 460 ml/min. It was shown that delignification by manganese gluconate with oxygen air under atmospheric conditions is very promising because can reduce energy consumption and ensure environmental safety. The value of kappa number was still high, but very interesting for further study because it operates at mild condition and uses green chemicals such as gluconic acid and oxygen air.

Keywords: lignocellulose pre-treatment, green delignification, oil palm empty fruit bunch, lignin, kappa number.

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Introduction

A lignocellulosic material consists of 35–50% cellulose, up to 35% hemicelluloses, 5–30% lignin and a slightly percentages of extractive [1]. Oil palm empty fruit bunch (OPEFB) as a lignocellulosic material is available abundantly in Indonesia, because this country is one of the world's largest producer of crude palm oil (CPO). Indonesia produced 43 million tons of CPO in 2019 [2]. The mill must «dump» 1–1.1 tons of OPEFB for each ton of CPO [3].

The hemicellulose, cellulose and lignin in lignocellulosic biomass are combined in a complex hierarchical structure, which makes pre-treatment steps show the most challenging of biomass utilization. Polysaccharides (cellulose and hemicellulose) are polymers of sugars which is fermentable sugar sources, whereas lignin can be used for production of chemicals [4]. Meanwhile, there are a lot of valuable products potentially obtained from lignin such as aromatic rich pyrolysis oil, mixed quinones, mixed benzylic aldehydes, mixed phenols, mixed aromatic alcohols, mixed organic acids, mixed hydrocarbons, alkyl benzenes, polymers, activated carbon and carbon fibres [5].

Lignin is an integral cell wall constituent in all vascular plants, including herbaceous varieties. Lignin provides rigidity, water-impermeability, and resistance against microbial attack. Lignin is an aromatic polymer consisting of guaiacyl-(G), syringyl-(S) and p-hydroxyphenyl-(H) phenylpropanoid units [6]. The differences of each unit are shown in Fig. 1.

Pre-treatment of lignocellulosic biomass is a necessary step to break the lignin and hemicellulose

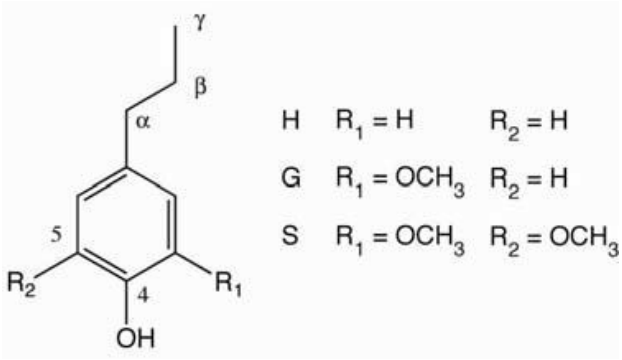

Fig. 1. Lignin phenylpropanoid units [6]

structure and makes polysaccharides easily available for enzyme digestion [7]. This process is known as delignification. Even though many research and development efforts have been carried out, the delignification is still one of the main obstacles to the availability of cellulose and hemicellulose.

Various ways of delignification that have been reported in the literature can be categorized into three groups of methods, namely physical, chemical, and biological. Physical treatment such as steam pre-treatment, which is carried out for several minutes, is a simultaneous treatment with high pressure and high temperature. NaOH-catalysed steam pre-treatment was incorporated for delignifying OPEFB [8]. Extremely dilute acid (EDA) by flow through pre-treatment was carried out as lignin removal pre-treatment [9]. The most common alkaline chemical pulping/delignification is a kraft lignin process which is carried out at high pH in sodium hydroxide and sodium sulphide at the temperatures of 423–453 K [10].

Some disadvantages of this method consist in need for a large supply of energy, causing waste and not atmospheric condition. Ion manganese or iron complexes (in oxidation state 200–1500 ppm) are used as catalysts to activate peroxo compounds in delignification. Transition metal complex compounds with polydentate ligands considerably surpass the delignifying and bleaching performance in the temperature range of 50–98^{0}C and reaction time of 45–120 minutes [11]. In addition, there is a delignification method that used lignin degrading enzymes namely manganese peroxide (MnP) produced by almost all wood-colonizing basidiomycetes causing white-rot and various soil-colonizing litter-decomposing fungi. In this process, MnP uses Mn^{2+} as the preferred substrate (electron donor). The Mn^{3+} formed is stabilized by organic acids, such as oxalate and acts as diffusible redox-mediator that attacks organic molecules via hydrogen and one-electron abstraction [12].

Catalyst Mn(II) sulphate with complexing agent (Na-gluconate) inhibits the undesirable peroxide decomposition that occurs in the presence of other manganese species independently of bleaching and providing significant improvement in stability over peroxide bleach catalysts based on dipositive Mn(II) [13]. Delignification used manganese acetate (MnOAc) and H_2O_2 caused degradation of the lignocellulosic matrix of poplar wood at room temperature within a few days [14]. Oxygen delignification has great potential for being the first stage of totally chlorine-free bleaching of OPEFB soda pulp which reducing kappa number about 50% on paper properties [15]. Sodium gluconate ($NaC_6H_{10}O_7$) and product of D-glucose complexes solubilize the +2, +3 and +4 oxidation states of manganese in strongly alkaline media [16]. Oxygen is a weak oxidizing agent in its normal state. Oxidation under atmosphere condition often requires alkaline conditions to ionize the free phenolic hydroxyl groups in lignin [17].

Although a lot of research about delignification, there are a few delignification research used manganese metal and air oxygen. The objective of this study is to evaluate the performance of lignocellulose pre-treatment with oxygen and ammoniac-ammonium sulphate solution catalysed by manganese gluconate complex at the temperatures below 343 K and pH of 8–9.5 with oxygen air. A good result of the performances of this delignification method will greatly save energy consumption.

Experimental

Materials

The chemicals used for delignification consisting of manganese sulphate from Merck, gluconic acid from Sigma Aldrich and OPEFB used as lignocellulosic material obtained from Mill local brand. Chemicals used for kappa number analysis were all analytical grade and consisting of potassium iodide, starch, sodium thiosulphate pentahydrate, potassium permanganate and sulfuric acid from Merck.

Soxhlet extraction for preliminary treatment of OPEFB

Before delignification, OPEFB is preliminary treated by using Soxhlet extraction to get rid of the extractive material. This process is expected to remove metal ions such as copper, iron, and cobalt. Such removal enhances the catalytic activity of the manganese compounds in delignification and retard a catalytic effect on the degradation reactions. This treatment implies washing of OPEFB with hot water at temperatures of 90–160^{0}C for 0.1 to 10 hours

[19], meanwhile this experiment operated at the temperature of 105^{0}C for 4 hours. Soxhlet extraction is carried out in a glass reactor connected to Soxhlet apparatus, which is heated up in a heating mantle.

Determination of extractive content is done by calculating the weight differences before and after Soxhlet extraction. Dry OPEFB that has been free from extractives is send to Balai Besar Pulp dan Kertas for analysing the composition of cellulose, hemicellulose, and lignin.

Delignification of OPEFB

The delignification involves seven following process variables: initial pH of ammonia-ammonium sulphate solution (8.5–9.5), reaction time (4–24 hours, i.e. 14400–86400 s), temperature (35–65^{0}C, i.e. 308–338 K), mass ratio Mn^{2+}/lignocellulose (0.033–0.33 wt.%), ratio soaking solution with mass of lignocellulose (25–50 ml/g, i.e. 0.025–0.05 m^3/kg), molar ratio gluconic acid/Mn^{2+} (15–76), and air flow rate (40.2–765.6 ml/min). The analysed parameter are weight loss of the OPEFB and kappa number after delignification. The influence of variables factor was studied by using fractional factorial experimental design $2^{(7-4)}$ [18].

Delignification experiments were carried out in a 250 ml three neck Erlenmeyer flask which was equipped with a heater, stirrer, assembled with reflux condenser, thermometer, and air injection channel. The delignification apparatus is shown in Fig. 2. At each run, 5 grams of OPEFB with particle size of 20 mesh which had been separated from extractives were delignified with air oxygen and manganese(II) gluconate complex in ammonia/ammonium sulphate buffer solution.

Fig. 2. The apparatus of OPEFB delignification

Analysis of kappa number

Kappa number is a measurement of amount of residual lignin in the pulp that related to degree of delignification of pulp. A low kappa number showed a low lignin content. The kappa number is the volume of the consumption of 0.1 N potassium permanganate solution by 1 g of dried pulp and the results are corrected to 50% consumption of the permanganate added. It was determined in accordance with the TAPPI Standard T 236 om-99 [20].

Results and discussion

Characterization of OPEFB

The experiments of Soxhlet extraction showed that the range of extractive composition in OPEFB is 14–16% (dry weight). The extractive free of OPEFB are analysed at Balai Besar Pulp dan Kertas by NREL TP-510-42618 method. The composition of extractive free of OPEFB consists of cellulose, hemicellulose and lignin as given in Table 1.

Table 1

Composition of OPEFB

Component	Content
cellulose	47.57 (w/w%)
hemicellulose	21.34 (w/w%)
lignin	34.82 (w/w%)

High content of cellulose showed that OPEFB has a big potential to be processed. The results of this analysis become a reference for the delignification process.

Delignification

Operating condition of delignification process follow factorial fractional experimental design $2^{(7-4)}$ obtained eight times experiment. Analysis parameters are weight loss of delignified OPEFB and the value of kappa number. Weight loss of delignified OPEFB is an indication of the amount of lignin that is dissolved into the soaking solution, while kappa number showed the amount of residual lignin in OPEFB. The kappa number showed that lignin remains in OPEFB. From these two parameters, a good response variable is shown by the highest weight loss of delignified OPEFB and the lowest kappa number value. Data of operating condition delignification and the analysis of the delignified OPEFB are presented in Table 2.

The data presented in Table 2 were processed by Montgomery (2001) calculation to analyse the most influential factor variables. The calculations were performed according to the following equation:

$$l_n = \frac{1}{4} \cdot \text{total run value},$$

Table 2

Operating condition of delignification and analysis of delignified OPEFB*

Run	A	B	C	D	E	F	G	Final pH	% ΔW_{OPEFB}	Kappa number
1	8.5	4	308	0.33	250	76:1	765.6	7.7	11.12	112.22
2	9.5	4	338	0.033	125	76:1	460.2	8.4	14.32	108.26
3	8.5	24	308	0.033	250	15:1	460.2	6.6	21.57	121.71
4	9.5	24	308	0.33	125	15:1	765.6	6.8	24.54	104.69
5	8.5	4	338	0.33	125	15:1	460.2	6.1	8.78	93.17
6	9.5	4	338	0.033	250	15:1	765.6	7.2	17.88	110.98
7	8.5	24	338	0.033	125	76:1	765.6	5.7	13.56	93.01
8	9.5	24	338	0.33	250	76:1	460.2	5.4	25.93	186.66

*Note: A=pH (initial); B=time (hour); C=temperature (K); D=mass ratio Mn^{2+} to OPEFB (%); E=soaking volume (ml); F=molar ratio gluconic acid/Mn^{2+}; G=air flow rate (ml/min).

where l_n is the effect of each variable.

The calculation result shows which process variable has the most influence on the percent weight loss of OPEFB and kappa number value.

The highest effect is the absolute value of the highest number. The graphs of the calculation results conducted by Minitab 17 software are presented in Figs. 3 and 4. Figure 3 is a bar graph that showed the effect value of each process variables, whereas Figure 4 is a graph of the effect of kappa number

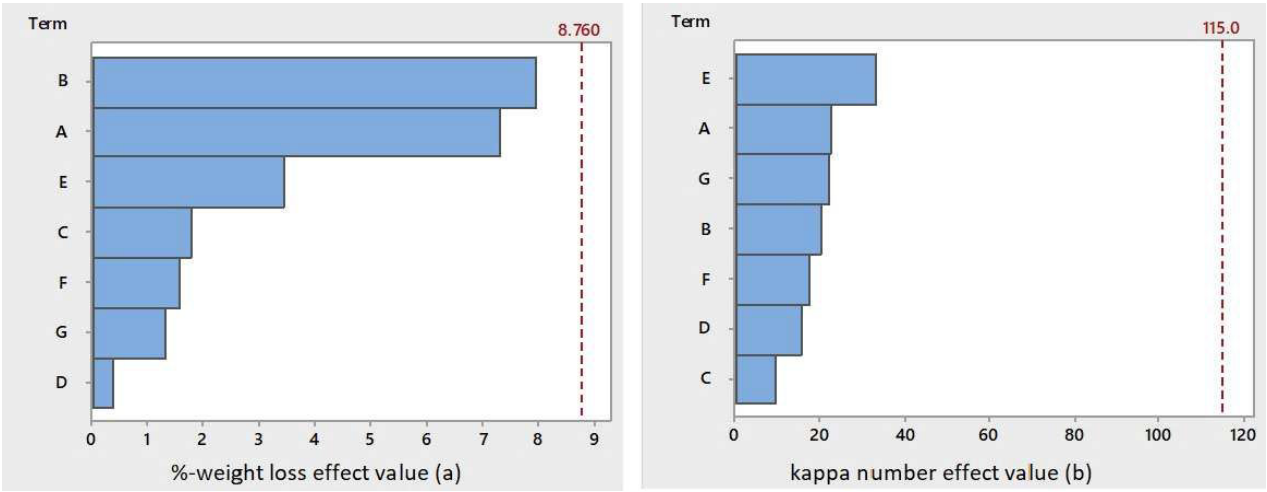

Fig. 3. Process variable effect after delignification

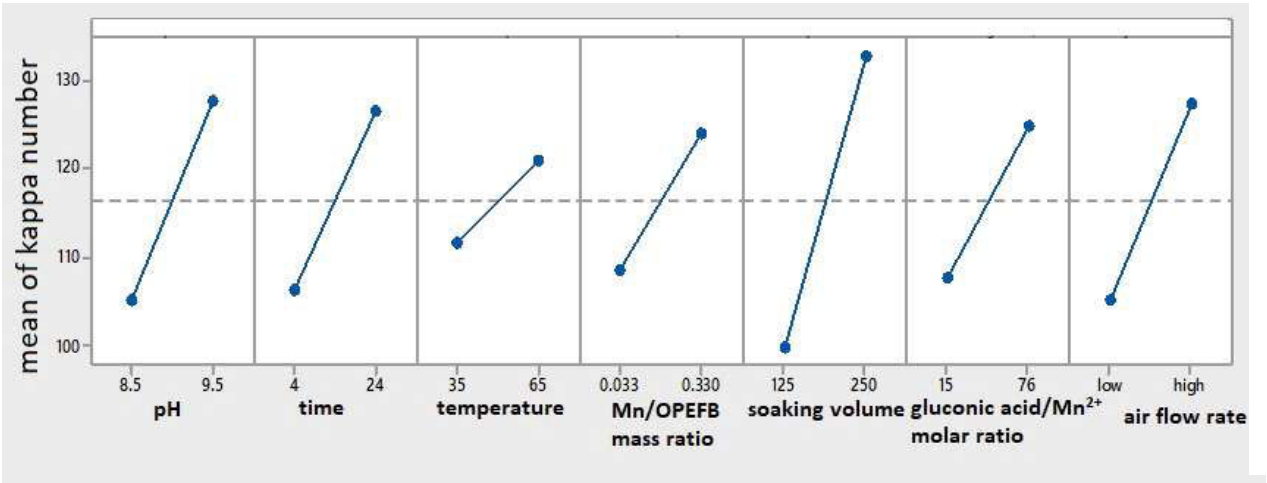

Fig. 4. Graphs of effects of different values on kappa number

value at low and high levels of each variables process.

Figure 3 showed that there is no correlation between %wt. loss and Kappa Number values. It can be seen from the sequence that a difference of the process variables effect value based on the %weight loss and kappa number is observed. The most influential process variable based on the %weight loss response variable is time (B). Meanwhile, the most influential process variable based on the kappa number is a ratio of soaking volume to the weight of OPEFB (E). This difference is due to the fact that the weight loss fraction of OPEFB is not only lignin but can also be hemicellulose or cellulose.

Based on a statistic showed in Fig. 3, the most influential process variables on weight loss are time (B), pH (A) and the ratio of soaking volume to the weight of OPEFB (E). The highest value of % weight loss was run 4 (24.54%) and run 8 (25.93%). The operating conditions of both runs were delignification time (24 hours) and pH (9.5). This showed that the longer time and the higher initial pH gave the greater % weight loss. It was also showed that the longer time and higher pH makes OPEFB higher chance of decomposition lignocellulose.

Figure 4 showed that the most influential process variables based on the kappa number are the soaking volume, pH and air flow rate. The volume of soaking solution at a low level (125 ml) gives a better effect (low kappa number value) as compared with the volume of the soaking solution at a high level (250 ml). The pH of the solution on the low level (8.5) also yields a better effect (low kappa number) than on the high level (9.5).

A lower air flow rate (460.2 ml/min) gave a better effect (low kappa number) compared to a higher flow rate (765.6 ml/min). A lower volume of soaking solution provides a better effect. It caused air oxygen penetration into OPEFB. At the same time, at higher soaking volume, air oxygen spreads into the solution rather than penetrates into OPEFB.

A lower pH value gave a better effect. This is due to manganese(III) in the form of gluconate complexes being more stable at pH 9–12 [13]. Based on this, it was thought that the manganese(III) gluconate complex is more stable at pH 9.5 than at pH 8.5. Therefore, manganese is easily reduced and oxidized again at pH 8.5. At pH 8.5, a reaction cycle occurres that produces hydrogen peroxide or other radicals that can continuously degrades lignin because it is more reactive. Whereas, at pH 9.5 the manganese(III) gluconate complex is more difficult to reduce again by the lignin compound to the manganese(II) gluconate complex because of its stability.

Kappa number increases with increasing the temperature because pH of solution decreasing faster at higher temperature. At lower pH, redox reaction between manganese(II) catalyst and oxygen yielding manganese(III) ions and hydrogen peroxide does not occur. Hydrogen peroxide is used to break lignin compound in OPEFB. pH is the most impactful variable in this process.

As far as the air flow rate response variable is concerned, better delignification happens when higher air is flowed. This shows that the higher air flowed, the more oxidation occurs. Chelating metals Mn(III) and carboxylic acids (such as gluconic acid) can react with each other and convert to alkyl radicals which causes spontaneous reactions to produce other radicals (such as superoxide) [12]. These radicals make lignin increasingly unstable. Air oxygen that is flowed not only oxidizes manganese(II) to manganese(III), but oxidizes the radicals which make lignin more easily degraded. Therefore, the air oxygen provides increased delignification.

Conclusions

Delignification by manganese gluconate with oxygen air under atmospheric conditions can be carried out under mild condition. It is indicated by kappa number value and weight reduction. The optimum delignification result based on kappa number values were run 5 (kappa number of 93.17) and run 7 (kappa number of 93.01) at pH 8.5 for 4 to 24 hours, and temperature of 338 K, mass ratio Mn^{2+} to OPEFB (%) of 0.33, volume soaking solution of 125 ml, molar ratio gluconic acid/Mn^{2+} of 15:1 and air flow rate of 460 ml/min. Optimization of pH of the solution, volume of soaking solution and air flow are recommended to reduce kappa number. The value of kappa number was still high but very interesting for further study. It is because this delignification can save great energy consumption and is environmentally friendly. For example, it operates under mild condition and uses green chemicals such as gluconic acid and oxygen air.

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ДЕЛІГНІФІКАЦІЯ ПУСТИХ ПЛОДІВ ПАЛЬМОВОЇ ПАЛЬМИ ЗА М'ЯКИХ УМОВ КИСНЕМ ПОВІТРЯ ТА ГЛЮКОНАТОМ МАРГАНЦЮ

Лідія Елізабет, Ронні Пурваді, Татанг Х. Соеравіджая

Пучок плодів олійної пальми (OPEFB) як лігноцелюлозний матеріал широко доступний в Індонезії, оскільки ця країна є одним із найбільших у світі виробників сирої пальмової олії. Попереднє оброблення лігноцелюлозної біомаси є необхідним кроком для руйнування структури лігніну та геміцелюлози і робить полісахариди легко доступними для перетравлення ферментами. Метою даного дослідження є оцінювання ефективності попереднього оброблення лігноцелюлози киснем повітря, що каталізується глюконатним комплексом марганцю при температурах нижче 343 K і pH 8–9,5. Експерименти з делігніфікації виконували в колбі реактора, яка обладнана нагрівачем, мішалкою, зворотним холодильником, термометром і каналом нагнітання повітря. Оптимальні результати делігніфікації на основі значень числа каппа були близько 93 при pH 8,5 протягом 4 годин і температурі 338 K, масовому відношенні Mn^{2+} до OPEFB (%) 0,33, об'ємному розчині для замочування 125 мл, молярному відношенні глюконова кислота/Mn^{2+} 15:1 і швидкістю повітряного потоку 460 мл/хв. Показано, що делігніфікація киснем повітря за допомогою глюконату марганцю в атмосферних умовах є дуже перспективною, оскільки дозволяє знизити споживання енергії та забезпечити екологічну безпеку. Значення числа каппа все ще було високим, але дуже цікавим для подальшого вивчення, оскільки він працює в легкому стані та використовує зелені хімічні речовини, такі як глюконова кислота та кисневе повітря.

Ключові слова: попереднє оброблення лігноцелюлози, зелена делігніфікація, пальмовий порожній пучок плодів, лігнін, число каппа.

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