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RESEARCH ARTICLE

THE EFFECT OF OZONATION, ULTRASONIC, AND HYBRID OZONATION-ULTRASONIC PRETREATMENT METHODS ON THE DELIGNIFICATION OF OIL PALM MESOCARP FIBERS

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Abstract

Oil palm mesocarp fiberis a by-product of the palm oil pressing process, which has great potential if used as a second-generation biofuel raw material. The main components of oil palm mesocarp fiber are cellulose, hemicellulose, and lignin commonly called lignocellulose. Cellulose is the most valuable component to be utilized in the bioenergy sector. However, the oil palm mesocarp fiber's lignin layer, which binds cellulose and restricts cellulose accessibility, makes it difficult to use. Ozone pretreatment is considered to be an alternative and effective method of lignin breakdown. This study compares the ozonation, ultrasonic, and hybrid ozonation-ultrasonicmethods used to degrade lignin in oil palm mesocarp fibers. The operating conditions were set at pH (3, 4, 5, 6, 7, 8, 9, 10, 11), flow rate (1, 2, 3, 4, 5) L min^{-1}, for (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100) minutes, at 29±1 ^{o}C. The research indicates that using ozonation-ultrasonic hybridization results in a more significant degradation of lignin than using ozonation and ultrasonics individually. In this investigation, the hybrid ozonation-ultrasonic treatment gives the best lignin degradation results and the highest quantities of cellulose, reaching 91.99% after 60 minutes at a temperature of 29±1 ^{o}C, a pH of 9, and a flow rate of 2 L.min^{-1}. Meanwhile, the degradation of lignin using ozone treatment is 72.75%, and ultrasound only 47.70%. Cellulose with the highest purity is 89.71%.

Introduction:-

Oil palm (Elaeis guineensis) is an African tropical rainforest plant. It is included in lignocellulosic biomass, which in recent years has received attention as a renewable energy source because of its abundant and sustainable availability. As a raw material, it has the potential to produce second-generation biofuels. Oil palm can thrive in countries such as Myanmar, Vietnam, Thailand, Colombia, Malaysia, Nigeria, and Indonesia (Mba et al., 2015)(Awalludin et al., 2015). A major producer of palm oil is Indonesia, followed by Malaysia(Foong & Ng, 2022)(Al-Sabaeei et al., 2022). The two most important palm oil producers are Indonesia and Malaysia, which produce 56.5% and 27.9% of the world's palm oil, respectively (Abdullah et al., 2020). The combined total palm oil production of the two countries reached 67.44 million tons in 2020, where this total production increased from the previous year, which was around 66.98 million tons per year(Parveez et al., 2021)(Directorate General of Plantations, 2021). The volume

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of waste will increase in tandem with the annual increase in palm oil production. During the processing of palm oil, peat mesocarp fiber waste is generated as a by-product, which is not included in the main product.

Mesocarp fiber from oil palm is lignocellulosic biomass which is the most significant waste from the palm oil industrial production process, accounting for about 22-24% of the mass of palm oil produced. (Pujokaroni et al., 2020). In large quantities, agro-residue or waste biomass of Oil Palm Mesocarp Fiber can cause disposal problems and pose a risk of environmental pollution. However, at the same time, lignocellulosic waste can be converted into a product that has added value because of its high cellulose content. Using this agro-residue does not create competition with human food needs (Ishfaq et al., 2022)(Verdini et al., 2021). About 50% of the components of the lignocellulosic biomass of oil palm fiber are cellulose, and the other 50% are cross-linked lignin and hemicellulose. Cellulose is an organic compound with more value from an economic standpoint because it can be used in several sectors, such as food, energy, medicine, textiles, paper making, and cosmetics(Megashah et al., 2018)(Candido & Gonçalves, 2019). Due to the cross-linking between hemicellulose and lignin, making cellulose is incapable of being converted into value-added products, making it more challenging to produce cellulose as a raw material (Perrone et al., 2016). Therefore, the pretreatment of palm oil fiber biomass waste is needed to extract cellulose and degrade lignin and hemicellulose components called the delignification process, thereby increasing the accessibility of cellulose and obtaining high-purity cellulose yields (Figure 1).

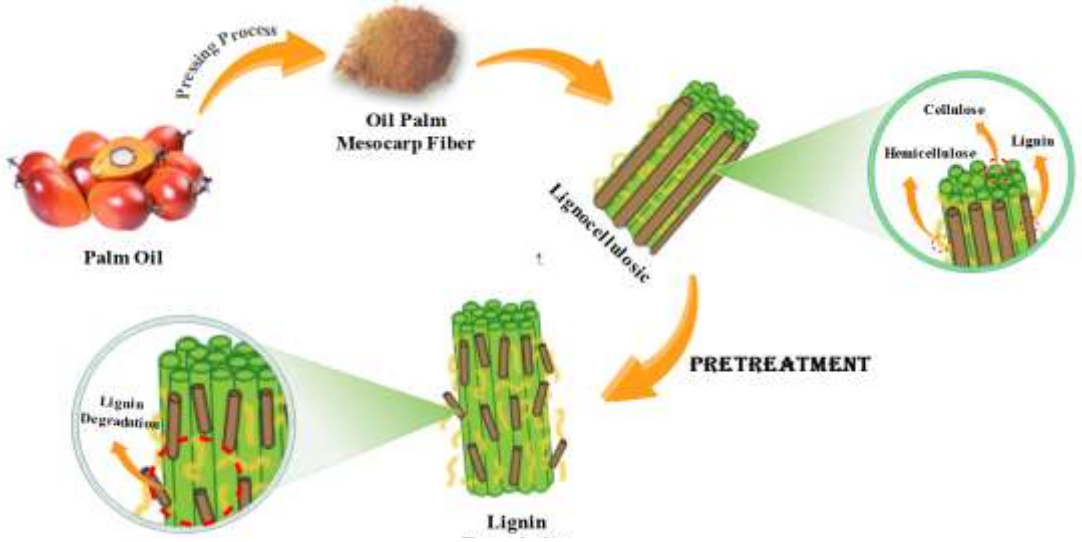

Fig.1:- Schematic of the Lignin Degradation Process.

Ozone is a powerful oxidizing agent and is environmentally friendly because it can decompose to produce oxygen so that it can be safely discharged into the environment and does not cause pollution(Omar & Amin, 2016)(Omar & Amin, 2021). Recently, many studies have explored the delignification method, namely pretreatment to degrade lignin components, using the ozone-based advanced oxidation process method. The ozone-based oxidation method has been shown to reduce the lignin component with little hemicellulose degradation and almost no change in cellulose (Perrone et al., 2016)(Li et al., 2015). However, this ozonation method has limitations, namely the low mass transfer of ozone due to the low solubility and stability in the liquid phase. Therefore, the ultrasonic method was added to increase ozone mass transfer. A cavitation phenomenon occurs during the ultrasonic process, resulting in the formation, growth, and collapse of microbubbles, which can increase the contact surface area of ozone with the biomass of oil palm mesocarp fiber, thereby increasing ozone mass transfer (Abdurahman & Abdullah, 2020). Additionally, the cavitation bubbles in the ultrasonic process can also accelerate the ozone decomposition process to produce more free radical compounds. The process is reflected in Equations 1 and 2 (Fu et al., 2019)(Kıdak & Doğan, 2018).

$$O_3 \xrightarrow{)))} O + O_2 \qquad (1)$$

$$O + H_2O \xrightarrow{)))} 2OH^* \qquad (2)$$

The free radical compounds produced have a potential oxidation value that is greater than the potential oxidation value of ozone (Table 1). A larger oxidation potential value results in a more significant and faster oxidation ability at low temperatures so that it can be better and more efficient in degrading lignin in oil palm fiber biomass(M'Arimi et al., 2020)(Trisanti et al., 2018). Shen et al., (2017)reported that the hybrid ozonation-ultrasonic method gave better efficiency in degrading X-3B red dye in wastewater than individually for the ozonation and ultrasonic methods. The red dye X-3B degradation efficiency in various methods was reported sequentially, namely ozonation-ultrasonic > ozonation > ultrasonic. Thus, Shen et al. study demonstrated that the hybrid ozonation-ultrasonic method could synergistically affect waste degradation.

Table 1:- Oxidation Potential Difference Value (M'Arimi et al., 2020).

Oxidizing	Oxidation Potential Value (EV)
Hydroxyl Radical	2.80
Ozone	2.08
Sulfate Ion	2.01
Manganate Ion	1.77
Hydrogen Peroxide	1.77
Chlorite Ion	1.57
Chlorine	1.36
Dichromate Ion	1.23
Oxygen	1.23

To our knowledge, studies comparing different lignin degradation pretreatment methods, such as ozonation, ultrasonic, and hybrid ozonation-ultrasonic pretreatment methods on oil palm fiber biomass, have not been widely reported. This study aims to study the effectiveness of ozonation, ultrasonic, and hybrid ozonation-ultrasonicpretreatment methods to degrade lignin in oil palm fiber biomass. The data from this study can be used in developing biomass pretreatment of oil palm mesocarp fiber to have a more economical value.

Material and Methods:-

Oil palm fiber biomass is obtained from oil palm companies. Water was used to clean the Oil Palm Mesocarp Fiber, then dried at a temperature of 100 ^{O}C for 24 hours to remove soil and other impurities. The oil palm mesocarp fiber that has been separated from impurities is then sieved with a size of 60 mesh. The pH value was altered from 3 to 11 using sodium hydroxide (NaOH) with a purity of > 99% (E. Merck Cat. No. 106498) and H_2SO_4 with a purity of 95% to 97% (E. Merck Cat No. 100731) to better understand the impact of pH on the amount of lignin breakdown in biomass.

Ozonation Process of Oil Palm Mesocarp Fiber

Ozonation treatment of palm fruit fiber was carried out using a glass reactor equipped with a gas sparger. The ozone gas used in this study was produced by an ozone generator (Dipo Technology Indonesia). Ozone production is carried out by passing between two electrodes with different potentials (30 kV). The experiment was carried out by diffusing ozone gas at a flow rate of 2 L.min^{-1} with a concentration of 82±5 ppm into the solution using a gas sparger. The pH of the solution varied at pH (3, 4, 5, 6, 7, 8, 9, 10, 11) by adding 0.1 M sodium hydroxide or 0.1 M sulfuric acids to the solution, the reaction proceeds over a period of time (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100) minutes and a temperature of 29±1 ^{o}C, while the weight of the oil palm fruit fiber biomass used is fixed, which is 15 grams. Then dried at 100 ^{o}C for 24 hours, and further analysis was carried out using the Chesson datta method to determine the percentage of lignin degradation.

Ultrasonic Process of Oil Palm Mesocarp Fiber

In order to perform the ultrasonic procedure on oil palm mesocarp fiber, an ultrasound krisbow type KLS 303365 (ultrasound bath) was used, which operates at 42 kHz and is cooled by a thermostatic water bath. The experiment was carried out at 29±1 ^{o}C for (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100) minutes, and vary the pH from pH (3, 4, 5, 6, 7, 8, 9, 10, 11) by adding 0.1 M sodium hydroxide or 0.1 M sulfuric acid to the solution. At the same time, the weight of the oil palm fiber biomass used was fixed, which was 15 grams. The mixture was filtered, and afterwards, the oven was used to dry the residue for 24 hours at 100 ^{o}C. Then, further analysis was performed using the Chesson data method to determine the percentage of lignin degradation.

Hybrid Ozonation-Ultrasonic Process of Oil Palm Mesocarp Fiber

Ozonation-ultrasonic treatment of oil palm fiber was carried out in a hybrid manner using a glass reactor equipped with a gas sparger and an ultrasound bath. An ozone generator creates the ozone gas needed in the hybrid ozonation-ultrasonic process (Dipo Technology Indonesia). The experiment was carried out by diffusing ozone at different ozone flow rates (1, 2, 3, 4, 5) $L.min^{-1}$ into the solution using a gas sparger together with ultrasonic irradiation, and the pH of the solution was set at pH starting from (3, 4, 5, 6, 7, 8, 9, 10, 11) by adding 0.1 M sodium hydroxide or 0.1 M sulfuric acids to the solution. The hybrid ozonation-ultrasonic process was carried out at susceptibility times (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100) minutes and a temperature of 29±1 ^{o}C, using a sample of oil palm fiber biomass at a constant weight of 15 grams. Then the residue was dried at 100 ^{o}C for 24 hours.

The iodometric titration method measured ozone concentration in the solution at each flow rate. The method of measuring ozone concentration was done by adding 0.15 grams of potassium iodide and 5 mL of 10% citric acid into the solution in a glass reactor. The 0.2% starch indicator (starch solution) to the solution was added until the solution turned purple. Titrate the solution with sodium thiosulfate (0.01 $mol.L^{-1}$) until it is colourless, and calculate the concentration using the following equation:

$$Ozon\ \ Concentration\ (ppm) = \left[V \times \frac{0{,}24}{v} \right] \times 1.000 \tag{3}$$

V denotes the volume of sodium thiosulfate at the titration's endpoint, as 1 mL of 0.01 $mol.L^{-1}$ solution has an equivalent amount of ozone as 0.24 mg, v is the volume of the solution being analyzed, and 0.24 is a constant since it is equivalent in weight to 0.24 mg (Pujokaroni et al., 2020). The concentration of ozone in solution at various flow rates (1, 2, 3, 4, 5) $L.min^{-1}$ was 69±3, 82±5, 76±2, 74±1, and 70±8 ppm, respectively. For further analysis of degraded lignin, an analysis was carried out using the Chesson data method.

Lignin Degradation Analysis

Initial characterization of oil Oil Palm Mesocarp Fiber needs to be done to determine the composition of cellulose, hemicellulose, and lignin in the initial raw materials. Analysis of degraded lignin in oil Oil Palm Mesocarp Fiber before and after pretreatment was carried out using the Chesson data method (Omar & Amin, 2021)(Lismeri et al., 2016). Chesson data is a gravimetric analysis method commonly used for measuring lignocellulosic content proposed by Chesson in 1978. The main step in this method is to remove extractives, followed by hydrolysis of hemicellulose with strong acids at room temperature, then hydrolyzed again with dilute acid at room temperature. And the last part of the insoluble component is lignin which is then corrected for ash content (Chesson, 1978).

The Chesson data method was carried out by weighing 1 gram of dry Oil Palm Mesocarp Fiber sample (weight a), then adding 150 mL of distilled water and heating at 100 ^{o}C for 1 hour. In an oven at 100 ^{o}C, the mixture was dried and weighed to a constant weight (weight b) after filtering and washing with hot aquadest. The solid was then subjected to an hour-long reaction with 150 mL of 1N H_2SO_4 at 100 ^{o}C. The residue was then dried in an oven, filtered, and rinsed with distilled water before being weighed to a constant weight (weight c), and the dried solid was incubated with 10 mL of 72% H_2SO_4 for 4 hours at room temperature, followed by 150 mL of 1N H_2SO_4 and 1 hour of refluxing the mixture. Then, the mixture was filtered and washed using aquadest, and the resulting residue was dried in an oven and weighed to a constant weight (weight d). The dried solids were then ashed using a furnace at 525 ^{o}C. The resulting ash is then considered to be a stable weight (weight e). Equations (4) to equation (7) can be used to determine the percentage of cellulose, hemicellulose, and lignin.

$$Cellulose \quad (\%) \quad = \left[\frac{c-d}{a} \right] \times 100\% \tag{4}$$

$$Hemicellulose \quad (\%) \quad = \left[\frac{b-c}{a} \right] \times 100\% \tag{5}$$

$$Lignin \quad (\%) \quad = \left[\frac{d-e}{a} \right] \times 100\% \tag{6}$$

$$Lignin Degradation (\%) \quad = \left[\frac{lignin\ before\ \ pretreatment - lignin\ after\ \ pretreatment}{lignin\ before\ \ pretreatment} \right] \times 100\% \tag{7}$$

where a is the initial dry weight of oil palm fiber sample (gr), b is the dry weight of sample residue refluxed with hot aquadest (gr), c is the weight of sample residue after refluxing with H_2SO_4 1 N (gr), d is the weight of sample residue after treatment with 72% H_2SO_4 (gr), and e is the weight of ash from sample residue (gr).

Results And Discussion:-

The Effect of Pretreatment Methods on Lignin Degradation of Palm Oil Mesocarp Fiber

The composition of oil palm fiber biomass before pretreatment was analyzed to ascertain the levels of cellulose, hemicellulose, and lignin in it. The Chesson data method was used for the analysis.The purpose of this study was to identify the most efficient pretreatment technique for lignin degradation and to evaluate how pretreatment processing duration affected overall lignin degradation. Table 2 shows the composition of oil palm mesocarp fiber biomass after ozonation, ultrasonic, and hybrid ozonation-ultrasonic pretreatment.

Table 2:- Composition of Oil Palm Mesocarp Fiber.

Pretreatment	Composition after pretreatment (%)			
	Cellulose	**Hemicellulose**	**Lignin**	**Ash**
Untreated Palm Fiber	37.12	29.72	28.70	4.46
Ultrasonic	62.32	19.57	13.97	4.12
Ozonation	72.89	15.26	7.82	4.03
Ozonation-Ultrasonic	89.71	4.49	2.30	3.50

Table 2 illustrates that the largest component of the fiber biomass of oil palm fruit is cellulose, which is 37.12%. Cellulose increased significantly in samples pretreated with hybrid ozonation-ultrasonic, reaching 89.71%, then cellulose also increased in ozonation pretreatment to 72.89% and slightly increased in ultrasonic pretreatment to 62.32%. During pretreatment of oil palm fiber biomass, lignin and hemicellulose degraded, increasing cellulose content. The results of degraded lignin from oil palm mesocarp fiber in various methods are presented in Figure 3.

Based on Figure 3, it can be seen that the hybrid ozonation-ultrasonic method can provide greater effectiveness in degrading lignin. The combination of hybrid ozonation and ultrasonic methods used simultaneously at operating conditions of pH 7 and temperature of 29±1 ^oC with a flow rate of 2 $L.min^{-1}$ can degrade lignin of palm fruit fiber up to 89.76%. Under the same operating conditions, ozonation and ultrasonic pretreatment methods only resulted in lignin degradation of 69.20% and 42.65%, respectively. The findings of this study are consistent with those Patil & Gogate (2015), where the combined method of ozonation and ultrasonic can be more efficient and significant in degrading the pollutant dichlorvos in wastewater when compared to the use of the ozonation and ultrasonic methods individually. Shen et al (2017) conducted additional research that the efficiency in degrading the red dye compound X-3B in wastewater was hybrid ozonation-ultrasonic > ozonation > ultrasonic. Prasetyaningrum et al. (Prasetyaningrum et al., 2019) revealed that combining ozonation and ultrasonic processes can provide more effective results in depolymerizing carrageenan compounds when compared to the ozonation and ultrasonic processes used individually.

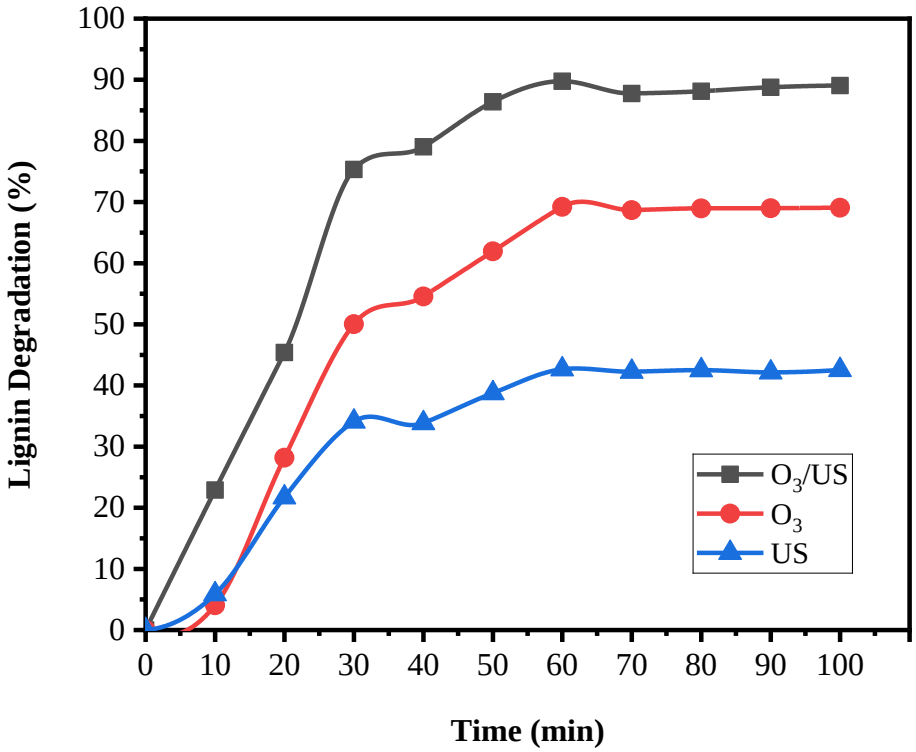

Fig. 2:- Lignin Degradation by Ozonation, Ultrasonic, and Hybrid Ozonation-Ultrasonic Methods.

Oxidation plays an important role in ozonation and ultrasonic processes. Some free radicals are formed in the process (Schramm & Hua, 2001). Sound waves with frequencies greater than 20 kHz on ultrasound produce rapid pressure cycles known as acoustic cavitation, which gives rise to intense vibrations in fluid systems (Perrone et al., 2016). Vibration in the liquid system produces microbubbles, which can boost ozone mass transfer into the solution and Increased hydroxyl radical levelsin the liquid phase so that it can provide a more significant degradation of lignin by breaking the lignocellulosic bonds in the Oil Palm Mesocarp Fiber biomass (Xiong et al., 2019). The lignin degradation process is also influenced by the length of time used in the pretreatment process of oil palm mesocarp fiber. Lignin degradation increased significantly in the initial 60 minutes of the pretreatment process, then remained constant after 60 minutes with the same operating conditions, namely at a temperature of 29±1 ^{o}C and pH 7 with a flow rate of 2 L.min^{-1}. This is because, in more than 60 minutes, the lignin content in the Oil Palm Mesocarp Fiber has degraded, so the rate of lignin degradation decreases.

The ozonation process, with a long reaction time in lignocellulosic biomass, also has the potential to degrade not only the lignin structure but can also degrade hemicellulose and amorphous cellulose. Similar results were reported in the study conducted by Omar et al. (Omar & Amin, 2016), where the degradation of lignin decreased after 60 minutes. This is because, after 60 minutes, most of the lignin layer has been degraded so that ozone can react with hemicellulose after the lignin layer. Barros et al. (Barros et al., 2013) also showed that after 60 minutes of ozonation time, hemicellulose was likely to undergo degradation, which was indicated by a decrease in the yield of xylose and glucose, which tended to be constant. Ramadoss and Muthukumar (Ramadoss & Muthukumar, 2016) also reported that there was no significant increase in the degradation of biomass lignin at the pretreatment time of 60 and 75 minutes. The holocellulose recovery and lignin degradation at 60 minutes was 88.37 ± 0.97% and 62.77 ± 0.66%, respectively, while at 75 minutes, the cellulose recovery and lignin degradation were 88.99 ± 0.23% and 61.2 ± 0.17%. These results indicate that the sonication time of 60 minutes is the optimum time for lignocellulosic biomass pretreatment. The same trend was also shown by Cubero et al. (García-Cubero et al., 2012), where the effectiveness of lignin degradation during the ozonation process did not increase significantly after 60 minutes of the reaction process. The research also observed that after 60 minutes of the ozonolysis reaction, ozone could attack the holocellulose components and could also form new products from the degradation of lignin, such as aromatic

aldehyde and hydroxycinnamic acids which could interfere with the hydrolysis process thereby inhibiting the utilization of cellulose.

Effect of pH on Lignin Degradation of Oil Palm Mesocarp Fiber

Pretreatment pH is one of the parameters that can determine the level of lignin degradation in lignocellulosic biomass. To comprehend how the lignin breakdown process is affected by the pH of the pretreatment, the pH was varied at pH ranges from 3 to 11 in each method. At each varying pH range, experiments were carried out under identical operating conditions, namely 29±1 ^{o}C for 60 minutes and 2 L.min^{-1}. The results of lignin degradation obtained in this study are presented in Figure 4. It was observed that under acidic conditions, the level of lignin degradation tends to be slightly lower than that of pretreatment under alkaline conditions in all methods. The best percentage of lignin degradation from the hybrid ozonation-ultrasonic, ozonation and ultrasonic method was obtained at pH 9-10, namely 91.88%, 72.75% and 51.32%. The hybrid ozonation-ultrasonic method of biomass pretreatment also showed the effectiveness of the two methods compared to the use of ozonation and ultrasonic methods individually at various pretreatment pH.

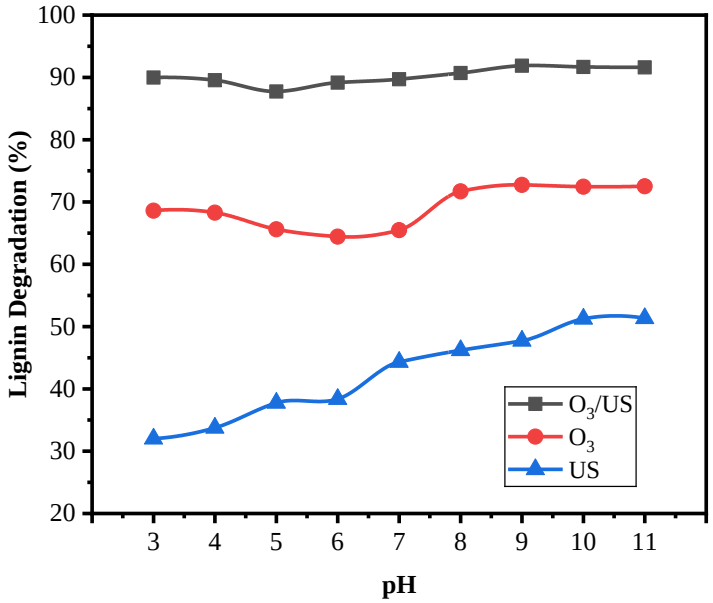

Fig. 3:- Effect of pH on Lignin Degradation.

The pH parameter in biomass pretreatment can affect the lignin oxidation mechanism used, leading to direct oxidation by ozone molecules or indirect oxidation by radicals (OH*). Under acidic conditions, the oxidation reaction of organic compounds is dominated by ozone molecules as oxidizing agents, while in alkaline conditions, the oxidation reaction is dominated by radical compounds (OH*), which are formed from the ozone decomposition process under alkaline conditions (Abdullah et al., 2020). The results of this study showed that the increase in pH did not significantly affect the degradation of lignin under the same operating conditions. However, the degradation of lignin in pretreatment with alkaline conditions resulted in a slightly larger degradation value when compared to pretreatment under acidic conditions. This is because in the pretreatment under alkaline conditions, the oxidation process takes place using a radical compound (OH*), which has a higher oxidation potential value compared to the potential oxidation value of ozone, while in acidic conditions, the lignin degradation reaction process is dominated by molecules. Ozone, thus pretreatment under alkaline conditions, can provide better lignin degradation.

The hybrid ozonation-ultrasonic method in various pH values from 3 to 11 in this study provided the highest lignin degradation value than the ozonation and ultrasonic methods used individually. Because the ultrasonic process used simultaneously with the ozonation process could provide the production of compounds. More radicals (OH*), thereby increasing the rate of Lignin degradation (Ladola et al., 2014). Similar results were also reported by Guo et al (2016) in their research showing that the rate of degradation of sulfamethoxazole organic compounds under alkaline conditions was higher than under acidic conditions. This happens because at a pH less than 7, the oxidation reaction process takes place dominated by ozone molecules. While sulfamethoxazole organic compounds are less

susceptible to ozone molecules, and on the other hand, the potential oxidation value of ozone is not greater than radical compounds (OH*), so reactions under acidic conditions can reduce the rate of degradation reactions. These results are also supported by research conducted by Shein et al. (Shen et al., 2017), that the degradation of organic compounds such as red dye X-3B increases along with the increase in pH. According to Wang et al., (Wang et al., 2012) the degradation of tetracycline increased as the pH value increased from 3 to 9 using ozonation pretreatment with ultrasonic treatment. Therefore, pH is a parameter that can be considered in the process because it can determine the mechanism of the course of an ozone oxidation reaction in degradation. On the other hand, the formation of radical compounds (OH*) also plays an important role in the indirect ozone oxidation process in the degradation process of lignocellulosic biomass.

Effect of Flow Rate on Lignin Degradation of Oil Palm Mesocarp Fiber

Pretreatment of mesocarp fiber biomass using the hybrid ozonation-ultrasonic method produces a synergistic effect in degrading lignin. The experiment was carried out by diffusing ozone at various ozone flow rates (1, 2, 3, 4, 5) $L.min^{-1}$ into a solution. The results obtained from the experiment were that the lignin composition decreased to increase the percentage of lignin degradation to reach 76.83%, 91.99%, 65.12%, 62.44%, and 48.05% at different flow rates (Figure 5).

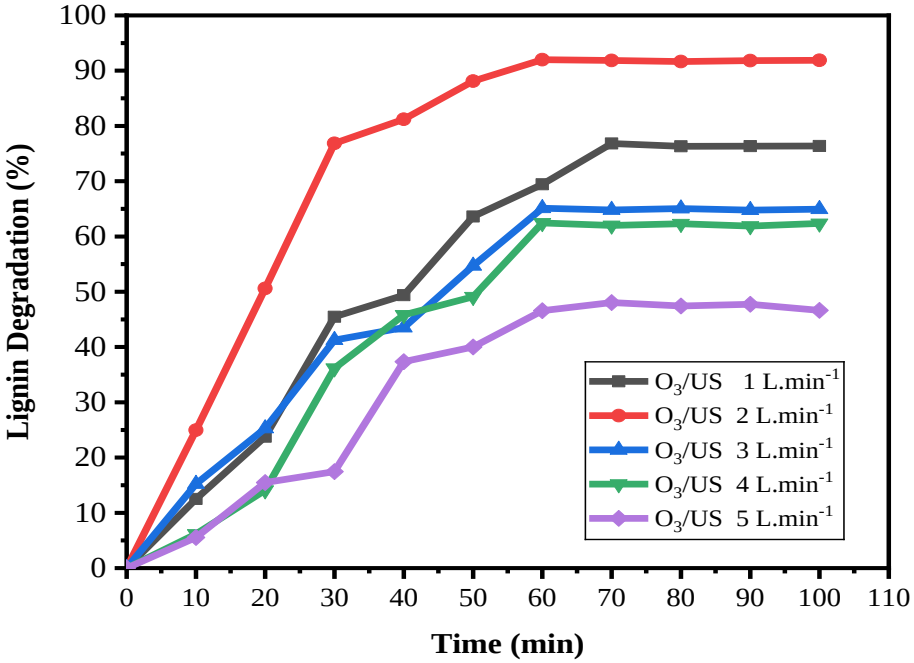

Fig. 4:- Ozone Flow Rate Effects on Lignin Degradation.

Increasing the flow rate of oxygen to 2 $L.min^{-1}$ increased the percentage of lignin degradation, then decreased after 2 $L.min^{-1}$. The decrease in lignin degradation occurs when the flow rate of ozone gas is greater. Hence, less ozone reaction is achieved when ozone gas stays in the reactor for a shorter period of time. The percentage of lignin degradation produced will be less because lignin can be degraded only in small amounts. Small. The findings of this study are consistent with previous findings by Ratnawati et al. (Ratnawati et al., 2018), where at flow rates between 2 and 4 $L.min^{-1}$, the ozone concentration increases and then decreases after that. The same findings were also reported by Boonduang et al. (Boonduang et al., 2012), who concluded that a 2 $L.min^{-1}$ flow rate provided the optimum concentration. The ozone flow gas encourages the increase to run faster so that it can reduce the use of reaction time. But at the same time, the increase in ozone flow rate makes ozone consumption higher, thus making the pretreatment process more expensive and will produce inhibitor compounds that will reduce the percentage of lignin degradation (Travaini et al., 2016).

The perspective of Oil Palm Mesocarp Fiber Pretreatment in Environmental Aspects

Oil palm mesocarp fiber is one of the most by-products produced from the pressing process in the production of palm oil in the palm oil industry. The availability of abundant mesocarp fibers creates problems in the surrounding

environment, especially if these by-products are not handled properly. It will produce a pile of products in addition to the oil palm mesocarp, which can create environmental problems. In line with the potential environmental problems that will arise from oil palm mesocarp fiber, mesocarp fiber is also one of the lignocellulosic biomass that can act as the best raw material for conversion into value-added products such as biofuel or biogas, paper, building blocks chemicals and adhesives. surfactant composite (Hongyan Chen et al., 2017)(Den et al., 2018).

The use of lignocellulosic biomass as raw material for value-added products, however, does not guarantee the production of valuable products without being followed by a good pretreatment process (Syaftika & Matsumura, 2018). The cross-linked lignin, hemicellulose, and cellulose components have the potential to block the accessibility of cellulose, thereby disrupting the economically viable biomass conversion process (Deralia et al., 2021)(Hongmei Chen et al., 2016). Ozonation and ultrasonic methods appear as environmentally friendly pretreatments and offer pretreatment processes that can reduce the use of chemicals that can pollute the environment by degrading lignin in biomass. The synergy of the two methods supports the efficiency of the degradation process. Besides that, in the pretreatment process using the ultrasonic-ozonation method, the remaining ozone will be decomposed into oxygen gas so that it does not have the potential to pollute the environment (Wang et al., 2019). Thus, it can be said that the pretreatment process of oil palm mesocarp fiber using the ultrasonic-ozonation method is a lignin degradation pretreatment method that is quite good in environmental aspects because it can reduce by-products from the palm oil industry and convert them into valuable products.

Conclusion:-

Lignin in oil palm fiber biomass can be efficiently degraded by ozone when ultrasonic irradiation is present. The use of the hybrid ozonation-ultrasonic method that is applied provides a synergistic effect in breaking down the lignocellulosic structure in oil palm mesocarp fiber so that it can produce greater lignin degradation when compared to the ozonation and ultrasonic methods used individually. The length of time used for pretreatment also plays an important role, where a significant increase in lignin degradation occurs in the initial 60 minutes of the pretreatment process and tends to remain after 60 minutes of pretreatment. In addition, the influence of pretreatment pH and ozone flow rate also affects the size and extent of lignin degradation. The largest lignin degradation in this study was obtained at 91.99% with a hybrid ozonation-ultrasonic treatment for 60 minutes at a temperature of 29±1 ^{o}C at pH 9 and a flow rate of 2 L.min^{-1}. In line with the results of lignin degradation, in this study, the operating parameters were the same, namely by applying the hybrid ozonation-ultrasonic process for 60 minutes at a temperature of 29±1 ^{o}C, pH 9 and flow rate 2 L.min^{-1}, producing cellulose with maximum content. This study's best results of lignin degradation reached 91.99%, and the highest cellulose content was 89.71%.

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References:-

1. Abdullah, M. A., Bahamid, A. A. A., Alshajrawi, O. M. S., Nazir, M. S., & Tahir, Z. (2020). Integrated Biomaterials Engineering of Oil Palm Fibres and Microalgae for Bioenergy, Environmental Remediation, and Conversion into Value-Added-Products. IOP Conference Series: Earth and Environmental Science, 448(1). https://doi.org/10.1088/1755-1315/448/1/012091
2. Abdurahman, M. H., & Abdullah, A. Z. (2020). Mechanism and Reaction Kinetic of Hybrid Ozonation-Ultrasonication Treatment for Intensified Degradation of Emerging Organic Contaminants in Water: A critical review. Chemical Engineering and Processing - Process Intensification, 154(February), 108047. https://doi.org/10.1016/j.cep.2020.108047
3. Al-Sabaeei, A. M., Al-Fakih, A., Noura, S., Yaghoubi, E., Alaloul, W., Al-Mansob, R. A., Imran Khan, M., & Aliyu Yaro, N. S. (2022). Utilization of Palm Oil and Its By-Products In Bio-Asphalt and Bio-Concrete Mixtures: A review. Construction and Building Materials, 337(January), 127552. https://doi.org/10.1016/j.conbuildmat.2022.127552
4. Awalludin, M. F., Sulaiman, O., Hashim, R., & Nadhari, W. N. A. W. (2015). An Overview of The Oil Palm Industry In Malaysia and Its Waste Utilization Through Thermochemical Conversion, Specifically Via Liquefaction. Renewable and Sustainable Energy Reviews, 50, 1469–1484. https://doi.org/10.1016/j.rser.2015.05.085

5. Barros, R. da R. O. de, Paredes, R. de S., Endo, T., Da Silva Bon, E. P., & Lee, S. H. (2013). Association of Wet Disk Milling and Ozonolysis As Pretreatment for Enzymatic Saccharification of Sugarcane Bagasse and Straw. Bioresource Technology, 136, 288–294. https://doi.org/10.1016/j.biortech.2013.03.009
6. Boonduang, S., Limsuwan, S., Kongsri, W., & Limsuwan, P. (2012). Effect of Oxygen Pressure and Flow Rate on Electrical Characteristic and Ozone Concentration of A Cylinder-Cylinder DBD Ozone Generator. Procedia Engineering, 32, 936–942. https://doi.org/10.1016/j.proeng.2012.02.035
7. Candido, R. G., & Gonçalves, A. R. (2019). Evaluation of Two Different Applications for Cellulose Isolated from Sugarcane Bagasse In A Biorefinery Concept. Industrial Crops and Products, 142(October). https://doi.org/10.1016/j.indcrop.2019.111616
8. Chen, Hongmei, Zhao, X., & Liu, D. (2016). Relative Significance of the Negative Impacts of Hemicelluloses on Enzymatic Cellulose Hydrolysis Is Dependent on Lignin Content: Evidence from Substrate Structural Features and Protein Adsorption. ACS Sustainable Chemistry and Engineering, 4(12), 6668–6679. https://doi.org/10.1021/acssuschemeng.6b01540
9. Chen, Hongyan, Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., & Han, S. (2017). A Review on The Pretreatment of Lignocellulose For High-Value Chemicals. Fuel Processing Technology, 160, 196–206. https://doi.org/10.1016/j.fuproc.2016.12.007
10. CHESSON, A. (1978). The Maceration of Linen Flax under Anaerobic Conditions. Journal of Applied Bacteriology, 45(2), 219–230. https://doi.org/10.1111/j.1365-2672.1978.tb04217.x
11. Den, W., Sharma, V. K., Lee, M., Nadadur, G., & Varma, R. S. (2018). Lignocellulosic Biomass Transformations Via Greener Oxidative Pretreatment Processes: Access to Energy and Value Added Chemicals. Frontiers in Chemistry, 6(APR), 1–23. https://doi.org/10.3389/fchem.2018.00141
12. Deralia, P. K., Jensen, A., Felby, C., & Thygesen, L. G. (2021). Chemistry of Lignin and Hemicellulose Structures Interacts With Hydrothermal Pretreatment Severity and Affects Cellulose Conversion. Biotechnology Progress, 37(5). https://doi.org/10.1002/btpr.3189
13. Directorate General of Plantations. (2021). National Leading Plantation Statistics 2019-2021 (In Indonesia). Angewandte Chemie International Edition, 6(11), 951–952.
14. Foong, S. Z. Y., & Ng, D. K. S. (2022). A systematic Approach for Synthesis and Optimisation of Sustainable Oil Palm Value Chain (OPVC). South African Journal of Chemical Engineering, 41(December 2021), 65–78. https://doi.org/10.1016/j.sajce.2022.05.001
15. Fu, L., Wu, C., Zhou, Y., Zuo, J., Song, G., & Tan, Y. (2019). Ozonation Reactivity Characteristics of Dissolved Organic Matter In Secondary Petrochemical Wastewater By Single Ozone, Ozone/H2O2, and Ozone/Catalyst. Chemosphere, 233, 34–43. https://doi.org/10.1016/j.chemosphere.2019.05.207
16. García-Cubero, M. T., Palacín, L. G., González-Benito, G., Bolado, S., Lucas, S., & Coca, M. (2012). An Analysis of Lignin Removal In A Fixed Bed Reactor By Reaction of Cereal Straws With Ozone. Bioresource Technology, 107, 229–234. https://doi.org/10.1016/j.biortech.2011.12.010
17. Guo, W. Q., Yin, R. L., Zhou, X. J., Cao, H. O., Chang, J. S., & Ren, N. Q. (2016). Ultrasonic-Assisted Ozone Oxidation Process for Sulfamethoxazole Removal: Impact Factors and Degradation Process. Desalination and Water Treatment, 57(44), 21015–21022. https://doi.org/10.1080/19443994.2015.1115373
18. Ishfaq Bhat, M., Shahi, N. C., Lohani, U. C., Singh, S., Sidique, Q., & Sirohi, R. (2022). Microwave Irradiation Assisted Intensive and Quick Delignification of Lignocellulosic Biomass, And Confirmation By Spectral, Morphological and Crystallinity Characterization. Bioresource Technology, 351(February), 127029. https://doi.org/10.1016/j.biortech.2022.127029
19. Kıdak, R., & Doğan, Ş. (2018). Medium-High Frequency Ultrasound and Ozone Based Advanced Oxidation for Amoxicillin Removal In Water. Ultrasonics Sonochemistry, 40, 131–139. https://doi.org/10.1016/j.ultsonch.2017.01.033
20. Ladola, Y. S., Chowdhury, S., Roy, S. B., & Pandit, A. B. (2014). Application of Cavitation In Uranium Leaching. Desalination and Water Treatment, 52(1–3), 407–414. https://doi.org/10.1080/19443994.2013.808792
21. Li, C., Wang, L., Chen, Z., Li, Y., Wang, R., Luo, X., Cai, G., Li, Y., Yu, Q., & Lu, J. (2015). Ozonolysis Pretreatment of Maize Stover: The Interactive Effect of Sample Particle Size and Moisture on Ozonolysis Process. Bioresource Technology, 183, 240–247. https://doi.org/10.1016/j.biortech.2015.01.042
22. Lismeri, L., Zari, P. M., Novarani, T., & Darni, Y. (2016). Synthesis of Cellulose Acetate from Cassava Stem Waste (In Indonesia). Jurnal Rekayasa Kimia & Lingkungan, 11(2), 82. https://doi.org/10.23955/rkl.v11i2.5407
23. M'Arimi, M. M., Mecha, C. A., Kiprop, A. K., & Ramkat, R. (2020). Recent Trends In Applications of Advanced Oxidation Processes (Aops) In Bioenergy Production: Review. Renewable and Sustainable Energy Reviews, 121, 109669. https://doi.org/10.1016/j.rser.2019.109669

24. Mba, O. I., Dumont, M. J., & Ngadi, M. (2015). Palm oil: Processing, Characterization and Utilization In The Food Industry - A review. Food Bioscience, 10, 26–41. https://doi.org/10.1016/j.fbio.2015.01.003
25. Megashah, L. N., Ariffin, H., Zakaria, M. R., & Hassan, M. A. (2018). Properties of Cellulose Extract from Different Types of Oil Palm Biomass. IOP Conference Series: Materials Science and Engineering, 368(1). https://doi.org/10.1088/1757-899X/368/1/012049
26. Parveez, G. K. A., Tarmizi, A. H. A., Sundram, S., Loh, S. K., Ong-Abdullah, M., Palam, K. D. P., Salleh, K. M., Ishak, S. M., & Idris, Z. (2021). Oil Palm Economic Performance In Malaysia and R&D Progress In 2020. Journal of Oil Palm Research, 33(2), 181–214. https://doi.org/10.21894/jopr.2021.0026
27. Patil, P. N., & Gogate, P. R. (2015). Degradation of Dichlorvos Using Hybrid Advanced Oxidation Processes Based on Ultrasound. Journal of Water Process Engineering, 8, e58–e65. https://doi.org/10.1016/j.jwpe.2014.10.012
28. Perrone, O. M., Colombari, F. M., Rossi, J. S., Moretti, M. M. S., Bordignon, S. E., Nunes, C. da C. C., Gomes, E., Boscolo, M., & Da-Silva, R. (2016). Ozonolysis Combined with Ultrasound as A Pretreatment of Sugarcane Bagasse: Effect on The Enzymatic Saccharification and The Physical and Chemical Characteristics of The Substrate. Bioresource Technology, 218, 69–76. https://doi.org/10.1016/j.biortech.2016.06.072
29. Prasetyaningrum, A., Jos, B., Dharmawan, Y., Ratnawati, R., Riyandita, S., & Scesario, R. (2019). Effect of pH on Depolymerization of κ-Carrageenan by Ultrasound, Ozone and Their Combination. Journal of Physics: Conference Series, 1295(1). https://doi.org/10.1088/1742-6596/1295/1/012061
30. Pujokaroni, A. S., Ohtani, Y., & Ichiura, H. (2020). Ozone Treatment For Improving The Solubility of Cellulose Extracted from Palm Fiber.Journal of Applied Polymer Science, 138(1), 1–11. https://doi.org/10.1002/app.49610
31. Ramadoss, G., & Muthukumar, K. (2016). Mechanistic Study on Ultrasound Assisted Pretreatment of Sugarcane Bagasse Using Metal Salt With Hydrogen Peroxide for Bioethanol Production. Ultrasonics Sonochemistry, 28, 207–217. https://doi.org/10.1016/j.ultsonch.2015.07.006
32. Ratnawati, R., Kusumaningtyas, D. A., Suseno, P., & Prasetyaningrum, A. (2018). Mass Transfer Coefficient of Ozone In A Bubble Column. MATEC Web of Conferences, 156, 2015–2018. https://doi.org/10.1051/matecconf/201815602015
33. Schramm, J. D., & Hua, I. (2001). Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism. Water Research, 35(3), 665–674. https://doi.org/10.1016/S0043-1354(00)00304-3
34. Shen, Y., Xu, Q., Wei, R., Ma, J., & Wang, Y. (2017). Mechanism and Dynamic Study of Reactive Red X-3B Dye Degradation By Ultrasonic-Assisted Ozone Oxidation Process. Ultrasonics Sonochemistry, 38, 681–692. https://doi.org/10.1016/j.ultsonch.2016.08.006
35. Syaftika, N., & Matsumura, Y. (2018). Comparative Study of Hydrothermal Pretreatment for Rice Straw and Its Corresponding Mixture of Cellulose, Xylan, and Lignin.Bioresource Technology, 255(November 2017), 1–6. https://doi.org/10.1016/j.biortech.2018.01.085
36. Travaini, R., Martín-Juárez, J., Lorenzo-Hernando, A., & Bolado-Rodríguez, S. (2016). Ozonolysis: An Advantageous Pretreatment for Lignocellulosic Biomass Revisited. Bioresource Technology, 199, 2–12. https://doi.org/10.1016/j.biortech.2015.08.143
37. Trisanti, P. N., Setiawan H.P, S., Nura'ini, E., & Sumarno. (2018). Sengon Wood Saws Through Ultrasonic Alkaline Delignification Process. Sains Materi Indonesia, 19(3), 113–119.
38. Verdini, F., Gaudino, E. C., Grillo, G., Tabasso, S., & Cravotto, G. (2021). Cellulose Recovery from Agri-Food Residues by Effective Cavitational Treatments. Applied Sciences (Switzerland), 11(10). https://doi.org/10.3390/app11104693
39. Wan Omar, W. N. N., & Amin, N. A. S. (2016). Multi Response Optimization of Oil Palm Frond Pretreatment by Ozonolysis. Industrial Crops and Products, 85, 389–402. https://doi.org/10.1016/j.indcrop.2016.01.027
40. Wan Omar, W. N. N., & Saidina Amin, N. A. (2021). Fractionation of Oil Palm Fronds (OPF) by Ozonolysis for Enhanced Sugar Production. Chemical Engineering Transactions, 83, 409–414. https://doi.org/10.3303/CET2183069
41. Wang, S., Wang, J., Wang, T., Li, C., & Wu, Z. (2019). Effects of Ozone Treatment on Pesticide Residues In Food: A Review. International Journal of Food Science and Technology, 54(2), 301–312. https://doi.org/10.1111/ijfs.13938
42. Wang, Y., Zhang, H., Chen, L., Wang, S., & Zhang, D. (2012). Ozonation Combined with Ultrasound for The Degradation of Tetracycline In A Rectangular Air-Lift Reactor. Separation and Purification Technology, 84, 138–146. https://doi.org/10.1016/j.seppur.2011.06.035
43. Xiong, X., Wang, B., Zhu, W., Tian, K., & Zhang, H. (2019). A review on Ultrasonic Catalytic Microbubbles Ozonation Processes: Properties, Hydroxyl Radicals Generation Pathway and Potential In Application. Catalysts, 9(1). https://doi.org/10.3390/catal9010010.