Pretreatment of Tropical Lignocellulosic Biomass for Industrial Biofuel Production: A Review

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Abstract. As energy demand increase with human activities, the practical solution this far is to use more fossil-based energy to meet those demand. Diminishing fossil energy reserves that can cause crisis and also the increasing price of fossil energy are the main challenges for the world, and are a big problem for developing countries. Environmental factors, sustainability, and national resilience are the main considerations for replacing fossil energy with non-fossil alternative energy such as solar energy, hydro energy, wind energy and biomass energy. Lignocellulosic biomass which is a waste from the agricultural industry, livestock industry waste, solid waste and other materials is the most abundant source of biomass that can be used to produce biofuels. In Indonesia, the most abundant sources are palm oil empty fruit bunches, corn stover, rice husks, rice straw, sugarcane bagasse, and coconut husk. Utilization of lignocellulosic biomass to be converted into energy requires pretreatment to change interactions between components found in plant cell walls. Pretreatment can remove physical and chemical barriers that make lignocellulosic material difficult to react and difficult to access by enzymes for the hydrolysis process. While the hydrolysis process is a vital stage in the biochemical process from lignocellulose to sugar-based energy conversion. By comparing several pretreatments based on glucose yield and other technical factors, it can be concluded that steam explosion is the best pretreatment by the reason of not requiring a small sizing on the biomass so that it is more energy efficient; not use chemicals; low water content causes energy saving; no degradation of cellulose and lignin so that sugar yields are higher and lignin can be recovered; and also the results of hemicellulose degradation can be separated by leaching and having economical value. The mechanism of the process that occurs in the steam explosion pretreatment is that high temperatures cause the release of acetyl groups on the hemicellulose structure which causes autohydrolysis to degrade hemicellulose; high temperatures cause steam to be acidic and degrade hemicellulose and hydrolyze some cellulose; sudden pressure drop causes redistribution of the lignin structure so that the lignin structure is not damaged and can be recovered; the loss of lignin and hemicellulose which blocks enzyme access to cellulose causes an increase in glucose yield during the enzymatic hydrolysis process. The steam explosion pretreatment method is not effective for hard biomass, but that raw material is more effectively processed using the alkaline method.

1. Background
Along with the increasing human need for energy to support daily activities and needs, the solution that is still effective today is to balance this need with more exploitation of fossil energy. It is a major challenge for the world, and a big problem for developing countries. Environmental, sustainability, and national resilience factors are the main considerations for replacing fossil energy with non-fossil alternative energy such as solar energy, hydroenergy, wind energy and biomass energy [1]. One example of biomass energy is biofuel. Biofuel is a derivative organic fuel derived from agricultural and forestry
Biomass. Biofuels are produced through biological processes and can be used to produce heat energy through combustion or other technologies. According to data from the International Energy Agency (IEA), biofuels currently meet 1.5% of global transportation energy needs as a result of increased research and production in the last 10 years [2]. Lignocellulosic biomass, which is waste from agricultural industry, livestock industrial waste, solid waste and other materials, is the most abundant source of biomass that can be used to produce biofuels.

Utilization of lignocellulosic biomass to be converted into energy is required pretreatment to change the interaction between components contained in plant cell walls. Pretreatment can remove physical and chemical barriers that make lignocellulosic materials difficult to react and difficult to access by enzymes for hydrolysis. Meanwhile the hydrolysis process is a key step in the biochemical process from lignocellulose to sugar-based energy conversion. The ease of the hydrolysis reaction can be achieved due to the increase in cellulose that can be accessed by enzymes through the dissolution of the hemicellulose and lignin components that coat the cellulose components in the lignocellulosic biomass source.

Pretreatment is the most critical step in the utilization of lignocellulosic biomass if a large conversion value is desired. The pretreatment principle that is currently most widely used is biological, chemical, and physical or chemical-physical pretreatment [3]. In general, the biggest challenge that arises in the pretreatment process is to achieve a process that is effective in terms of costs, can be applied at an industrial scale as well as an environmentally friendly production process [4].

2. Biofuel

Biofuel can be defined as organic fuel derived from agricultural biomass through a biological process and can be used as thermal energy in combustion technology. The world has recently been intensifying the production of new and renewable energy to reduce waste. Biofuel production itself is now more desirable because it is lightweight, cheap, produces higher energy, and produces less pollution.

In 2012, the estimated consumption of petroleum reached 89 million barrels per day of which about half was used for gasoline. It is predicted that for the next 50 years, the fossil fuels used to date will be exhausted. Therefore, at this time, biofuel can be used as a solution to this problem because of its nature that comes from renewable biomass. At this time there are many technologies that can use foodstuffs to process it into energy. However, there is a conflict because the first generation products will shift human food needs, so that the second and third generations are chosen which do not come from human food needs that come from grass, agricultural waste, and algae. Examples of waste that can be used in the second generation include urban solid waste, used cooking oil, industrial waste, agricultural waste, and sludge waste. The products of this second generation are biodiesel, bioethanol, biomethanol and biogas. Recently, second and third generation biofuels are more profitable than first generation biofuels because they come from agricultural residues and algal biomass.

From the various kinds of biomass that can be used for biofuel production, annual biomass production worldwide reaches 220 billion dry weight tons or the equivalent of 4500 EJ (Exa Joule) of solar energy captured annually. From that production, approximately 270 EJ comes from renewable biomass. The rest comes from wood waste, wood, agricultural waste, and waste from animals. In global data, there are 4 main agricultural producing sectors, namely wheat, maize, rice and sugarcane, where the four crops produce the most biomass. The four plants produce a total biomass of 5358.54 million tons of dry biomass per year. Even though many of these agricultural wastes are just burned for free.

3. Lignocellulosic Biomass

Lignocellulosic biomass is biomass derived from plants with the main components of cellulose, hemicellulose, and lignin. The three of them form a complex chemical bond that forms the basis of plant cells. In general, the composition of lignocellulosic ingredients is cellulose (30-50%) hemicellulose (20-30%) and lignin (10-25%). Indonesia itself is a country with a tropical climate and has various types of plants. In the agricultural sector, a lot of agricultural waste is wasted even though this waste has the potential to be reused, especially being processed again into energy.
3.1. **Coconut Husk**

Coconut is a plant that lives in many tropical areas, one of which is Indonesia. According to the Directorate General of Plantation (2016), coconut production in Indonesia reaches 2,890,735 tons per year. This high coconut production is accompanied by high production of biomass waste in the form of coconut husks. The coconut coir is the outermost part of the coconut. When the coconut fruit is separated from the coir, it will get 35% of the coconut weight [7]. It is estimated that the production of coconut coir produced is 1,011,757.25 tons in 2016. Coconut coir is a biomass containing crude fiber composed of lignocellulosic compounds. The content of cellulose and lignin in coconut husk is very large, namely 41.19% lignin and 26.72% cellulose, while for hemicellulose it is 17.73% [6].

3.2. **Sugarcane bagasse**

Sugarcane is an agricultural plant that is often found in Indonesia, especially on the island of Java. Sugarcane is a raw material for sugar that comes from the extract of these plants. Sugarcane in Indonesia is one of the top ten producers in the world, where Indonesia was able to produce 29 million tons of sugarcane in 0.41 million hectares of sugarcane in 2012[7]. Sugarcane consists of 3 main parts, namely sugar extract, molasses and bagasse. Molasses is a co-product of sugar which can be used in the production of ethanol. In sugarcane, 5% of the content is sugar and 90% of the content is bagasse, where in the bagasse there is cellulose (52%), hemicellulose (20%), and lignin (24%) [8].

3.3. **Rice Husk**

Rice is the largest agricultural commodity in Indonesia. The consumption of rice in Indonesia in 2005 reached 54 million tons. From this amount, 10.8 million tons of rice husk can be produced.[9]. According to another theory, the rice milling process usually yields about 20-30% of husk, 8-12% of bran, and 50-63% of milled rice [10]. Rice husks usually contain cellulose (42.2%), hemicellulose (18.47%), lignin (19.4%), and ash (15%) [11]. Meanwhile, rice straw contains cellulose (43%), hemicellulose (26%), lignin (12%), and ash (13%).

3.4. **Corn stover**

Corn (Zea Mays) is an important food crop in Indonesia. In 2006, the harvested area for maize in Indonesia was 3.5 million hectares with an average production of 3.47 tons / ha, and national maize production was 11.7 million tons. From these agricultural products, there is also waste from these crops with a production of 3.46 tonnes / ha in the form of waste stems and dry leaves. So that the total agricultural waste ranges from 12.1 million tons [12]. The content contained in corn waste is cellulose (37.1%), hemicellulose (22%), arabinan (2.5%), galactan (1.6%), lignin (20.7%), protein (7.8%), and others [13].

3.5. **Palm oil empty fruit bunch**

Palm oil (Alaeis guineensis) is the main raw material for palm oil production. Indonesia is the second largest palm oil producing country in the world. The number of oil palm plantations in Indonesia reaches 6,735,300 hectares spread across 22 provinces in Indonesia. The entire land can produce around 31,070,000 tonnes of palm oil per year. As much as 25-26% by weight of the total oil palm production is empty bunches and becomes waste. Only 10% of the empty bunches are used as fuel for boilers and compost, so there are still 7,130,565 tons of lignocellulosic biomass waste that has the potential to be a useful products. The content of oil palm empty bunches is 33.25% cellulose, 23.24% hemicellulose, 25.83% lignin, 56.49% holocellulose, 8.56% water, and 4.19% are extractive substances [14].

4. **Lignocellulose**

Lignocellulose is the main component in plant cell walls that form structures in plants. Lignocellulose mainly consists of cellulose, hemicellulose, lignin, pectin and glycosylated protein. Lignocellulose forms a complex crystal structure that is held together by covalent bonds, intermolecular bridges and Van Der Waals forces so that it is insoluble in water and resistant to enzyme action [15].
Cellulose is a straight chain polymer consisting of glucose $\beta$ (1 $\rightarrow$ 4) which are bonded to each other. In cellulose, there are amorphous and crystalline structures. The crystal structure of cellulose causes denaturation of cellulose into simple sugars requiring effort. Cellulose is not easy to dissolve in a solvent because it is fibrous and the have hydrogen bonds. In the pretreatment process, cellulose will be degraded into glucose. Glucose derived from cellulose can be degraded thermally during biomass pretreatment. In this degradation process, glucose is first dehydrated to HMF (5-hydroxymethyl-2-furaldehyde) which can then be further degraded into formic acid and levulinate acid [16].

Hemicellulose is a complex amorphous polymer with branched chains. Both chemically and structurally, hemicellulose is closely related to cellulose. The difference between hemicellulose and cellulose can be seen from the type and number of monosaccharides that compose them. The monosaccharides that make up hemicellulose consist of glucose, manose, galactose, xylose (the most) and arabinose. Hemicellulose is easier to denature compared to cellulose because hemicellulose does not have a crystalline structure [15]. During the pretreatment process, hemicellulose will be hydrolyzed into its constituent monosaccharides. Monosaccharides from hemicellulose can be further degraded into HMF (5-hydroxymethyl-2-furaldehyde), furfural, formic acid and levulinic acid [16].

Lignin is a polymer consisting of branched phenolic compounds. In plant cell walls, lignin acts as an adhesive for cellulose and hemicellulose. Some of the structural components of lignin are alcohol, methoxyl groups, phenolic, hydroxyl and aldehydes [15]. Because of the presence of lignin which has a negative role in monosaccharide production, the lignin bonds in biomass need to be broken. The pretreatment process can break the lignin bonds in lignocellulose. During the pretreatment process, lignin will be degraded into compounds that are inhibitory in biochemical processes. Lignin will be degraded into phenol or acetic acid compounds. This degradation product depends on the monomer compounds that make up lignin [16].

5. Biofuel industry
The massive increase in air pollution, the scarcity of petroleum sources and the increasing world oil price has created interest for countries in the world in exploring renewable energy sources. One sector that can apply renewable energy sources is the transportation sector by replacing fossil fuels with biofuels. Biofuels can be divided into bioethanol, biodiesel, biomethanol, biogas and biohydrogen. The types of biofuels most commonly produced on an industrial scale are bioethanol and biodiesel [17]. Bioethanol and biodiesel are the most important commodities in the world biofuel trade with an estimated 75% being bioethanol and 25% being biodiesel of the total biofuel sales. 50% of the world's bioethanol is supplied by America, 39% by Brazil and 5% by Europe [18]. Bioethanol is ethanol produced through biological means by converting biomass into bioethanol through biochemical processes such as hydrolysis or fermentation. The biomass used can be in the form of grains, lignocellulose and algae [19].

As one of the high cost processes, pretreatment also determines the amount of sugar yield that biomass can produce in the enzymatic hydrolysis process. The sugar yield in the enzymatic hydrolysis process without pretreatment is usually lower than 20%, while with pretreatment it can increase to more than 90% [23]. After pretreatment, the next processes are hydrolysis and fermentation, both processes can be carried out simultaneously or separately. Bioethanol production technology from lignocellulosic biomass has developed rapidly. However, there are still some unsupportive challenges in terms of cost effective and competitive production that prevent commercialization [24]. Some of these challenges are: difficulty in pretreatment, efforts to reduce enzyme costs, development of yeast that is more resistant to inhibitors and efforts to reduce capital costs in making complex production processes [25]. The way to reduce ethanol production costs on an industrial scale is by reducing raw material costs, increasing efficiency and production capacity and developing better production methods [26]. Pretreatment is the main challenge to get the best sugar raw material for the hydrolysis and fermentation process of lignocellulosic biomass. The resulting effect is not only at the level of the lignocellulosic component, but also at the tissue and cell level of the lignocellulosic biomass [27]. Efforts are being made to develop a pretreatment so that the result is lignocellulosic biomass with a greater surface area and porosity and
makes cellulose more accessible to enzymes by eliminating disturbing components [28]. The various
types of pretreatment available have their respective advantages and disadvantages for industrial scale
applications. Based on the relevant literature, the overall efficiency of pretreatment is by looking at the
balance between the formation of inhibitors and the solubility of biomass [29]. In addition, pretreatment
is one of the processes that greatly determines economic value in terms of obtaining reducing suga[30].
So that to commercialize production into an industrial scale pretreatment that is efficient, economical
and produces little inhibitor is needed.

6. Effectivity of pretreatment
The lignin layer forms a protective layer that surrounds cellulose and hemicellulose, and protects these
polysaccharides from enzymatic degradation. However, in the formation of reducing sugars, the
cellulose and hemicellulose compounds should be available in a free state without being protected by
other compounds so that the enzymatic process runs perfectly so that the sugar can be formed. So that
in the next process, sugar can be fermented into derivative products such as bioethanol or biomethane.
Therefore, the pretreatment process needs to be done to remove the lignin layer, reduce the crystallinity
of cellulose and increase the surface area to increase enzyme activity to produce reducing sugars. Apart
from being used as a reducing sugar product, a lignocellulosic biomass can produce a derivative product
that has a high selling value, namely bioethanol and biogas. In the production process, the most decisive
process can be the formation of a derivative product, as well as the amount of yield produced. A
pretreatment process has an important role, this is because in producing a high product, it is necessary
to have a strategy for selecting a pretreatment process, both in determining the process (psycochemical,
chemical, thermal, biological), as well as the operating conditions of the pretreatment process.

In determining the strategy in selecting the type of pretreatment, several considerations /
considerations are needed in order to produce the best and cheapest process. The following are factors
that are considered in selecting the pretreatment process:
• High yield for various types of raw materials
• The pretreatment results are easy to process
• No sugar degradation
• Few inhibitors
• No need for size reduction
• Rational operating conditions and low costs
• Less solid waste
• Effective in dry conditions
• Fermentation ability
• Recovery Lignin

From literature review here are the result of many experiment with different method and different
source of lignocellulosic biomass:

| No. | Method                  | Raw Material            | Treatment                      | Result                                      | Source |
|-----|-------------------------|-------------------------|--------------------------------|---------------------------------------------|--------|
| 1   | Mechanical pretreatment | Sugarcane bagasse       | Vibratory Ball Mill 15 Hz for 3 hours | Cellulose conversion 95.2%, Sugar yield 37.5%, Crystallinity decrease from 64.5% to 2.5% | [31]    |
| 2   | Mechanical pretreatment | Palm oil empty fruit bunch | Ball Mill 250 rpm for 2 hours | Cellulose conversion 62.4%, Sugar yield 39.36%, Crystallinity decrease from 56.1% to 9.3% | [32]    |
| Step | Pretreatment Method | Feedstock | Conditions | Conversion and Yield (%) |
|------|---------------------|-----------|------------|--------------------------|
| 3    | AFEX pretreatment   | Rice Straw| Temperature 80-90°C, moisture content 20-60%, ammonia to biomass ratio 0.1-2:1 | Cellulose conversion 80%, Hemicellulose conversion 80%, Sugar yield 48.2% |
| 4    | AFEX pretreatment   | Rice Straw| Pressure 94.8-158 Mpa, Amonia loading 1:1, moisture content 60%, residence time 15 minutes | Cellulose conversion 93%, Hemicellulose conversion 48%, Sugar yield 48.1% |
| 5    | AFEX pretreatment   | Palm oil empty fruit bunch | Temperature 135°C, residence time 45 minutes, moisture content 1:1-1.5:1 | Cellulose conversion 58%, Hemicellulose conversion 66%, Sugar yield 34.6% |
| 6    | Ozonolysis pretreatment | Sugarcane bagasse | Flowrate ozone 60L/hours for 45-195 minute | Hemicellulose conversion 41.7%, Sugar yield 32.17% |
| 7    | Microwave pretreatment | Corn stover | Temperature 180°C, frequency 2450 MHz, residence time 2 minutes | Cellulose conversion 24.1%, Hemicellulose conversion 17.2%, Sugar yield 8.73% |
| 8    | Microwave pretreatment | Rice husk | Temperature 180°C, frequency 2450 MHz, residence time 2 minutes | Cellulose conversion 22.8%, Sugar yield 8.5% |
| 9    | Microwave pretreatment | Corn stover | Power 800 W for 5 minutes | Cellulose conversion 27.8%, Sugar yield 6.7% |
| 10   | Ultrasound pretreatment | Corn stover | Temperature 80°C, frequency 40 kHz, Liquid Solid ratio 13:1, 30 minutes residence time | Hemicellulose conversion 90% |
| 11   | Acid hydrolysis pretreatment | Corn stover | Temperature 135-150°C, H₂SO₄ 0.73%, 34 minutes residence time | Cellulose conversion 78%, Hemicellulose conversion 97% |
| 12   | Acid hydrolysis pretreatment | Corn stover | HCl 1%, temperature 100-130°C, residence time 20-40 minutes. | Sugar yield 68.5% |
| 13   | Acid hydrolysis pretreatment | Sugarcane bagasse | H₂SO₄ 1-5%, residence time 30-90 minutes, biomass loading 7.5-11.25 | Sugar yield 58.1% |
| 14   | Acid hydrolysis pretreatment | Coconut husk | H₂SO₄ 2.5%, Temperature 105.8°C |  |
|   | Pretreatment Method       | Feedstock          | Reagent and Conditions                                                                 | Cellulose Conversion % | Sugar Yield % |
|---|--------------------------|--------------------|----------------------------------------------------------------------------------------|------------------------|---------------|
| **15** | Alkaline hydrolysis pretreatment | Sugarcane bagasse | **NaOH 1-5M. Temperature 25 - 50 °C. Residence time 16 hours**                          | 85%                    | 42.64%        |
| **16** | Alkaline hydrolysis pretreatment | Corn stover        | **NaOH 0.06 g/g biomass. Temperature 99 °C. Residence time 1 hour**                    |                        | 78.3%         |
| **17** | Alkaline hydrolysis pretreatment | Coconut husk       | **NaOH 20 - 30%, temperature 100 °C, residence time 2 - 3 hours**                      |                        | 45.6%         |
| **18** | Alkaline hydrolysis pretreatment | Coconut husk       | **NaOH 4%, Temperature 33.79 - 76.21 °C, residence time 0.59 - 3.41 hours**           |                        | 70.1%         |
| **19** | Alkaline hydrolysis pretreatment | Coconut husk       | **NaOH 1%, temperature 80 °C, residence time 16 hours**                                |                        | 27%           |
| **20** | Organosolv pretreatment   | Rice straw         | **Reagent Ionic Liquid cholinium arginate, temperature 90 °C, residence time 12 hours** | 75.2%                  | 21.2%         |
| **21** | Organosolv pretreatment   | Sugarcane bagasse  | **Reagent Ionic Liquid cholinium arginate, temperature 90 °C, residence time 12 hours** | 65.5%                  | 20.0%         |
| **22** | Organosolv pretreatment   | Rice straw         | **Reagent Ionic Liquid EMIM Acetate, temperature 130 °C, residence time 24 hours.**    |                        | 97%           | 40.93%        |
| **23** | Organosolv pretreatment   | Sugarcane bagasse  | **Reagent Ionic Liquid EMIM Acetate, temperature 145 °C, residence time 15 minutes.**  |                        | 69.7%         |
| **24** | Organosolv pretreatment   | Palm oil empty fruit bunch | **Reagent Ionic Liquid EMIM Acetate, temperature 90-130 °C, residence time 2 hours.** |                        | 96.6%         | 52.1%         |
| No. | Pretreatment Method          | Feedstock                | Severity | Conversion/Yield | Reference |
|-----|------------------------------|--------------------------|----------|------------------|-----------|
| 25  | LHW pretreatment            | Corn stover              | 3.9      | 55.9%            | [50]      |
| 26  | LHW pretreatment            | Coconut husk             | 3.25     | Sugar yield 20.6%| [51]      |
| 27  | LHW pretreatment            | Coconut husk             | 6.1      | Sugar yield 11.7%| [52]      |
| 28  | Steam explosion pretreatment| Rice straw               |          | Cellulose conversion 97.7%, Sugar yield 44.5%| [53]      |
| 29  | Steam explosion pretreatment| Sugarcane bagasse        |          | Cellulose conversion 96.4%, Sugar yield 50.12%| [54]      |
| 30  | Steam explosion pretreatment| Corn stover              |          | Cellulose conversion 93.3%, Sugar yield 36.24%| [55]      |
| 31  | Steam explosion pretreatment| Coconut husk             |          | Sugar yield 37.8%| [56]      |
| 32  | Steam explosion pretreatment| Palm oil empty fruit bunch|          | Cellulose conversion 47%, Sugar yield 15.62%| [57]      |
| 33  | Supercritical CO<sub>2</sub> pretreatment| Corn stover              |          | Cellulose conversion 77.8%, Sugar yield 23.3%| [58]      |
| 34  | Supercritical CO<sub>2</sub> pretreatment| Corn stover              |          | Sugar yield 30%| [59]      |
| 35  | Supercritical CO<sub>2</sub> pretreatment| Palm oil empty fruit bunch|          | Sugar yield 24%| [60]      |
| 36  | Supercritical CO<sub>2</sub> pretreatment| Palm oil empty fruit bunch|          | Cellulose conversion 72%, Sugar yield 23.94%| [61]      |
| 37  | Biological pretreatment     | Corn stover              |          | Sugar yield 32.2%| [62]      |
residence time 48-72 hours

| No | Biological pretreatment | Corn stover | White-rot fungal, incubation temperature 28°C for 30 days | Sugar yield 39.4% |
|----|-----------------------|-------------|--------------------------------------------------------|-------------------|
| 38 | [5]                    |             | T. Hirsuta yj9, incubation temperature 30 °C for 7 - 42 days in dark environment. | Sugar yield 74%   |

6.1. Mechanical pretreatment
Mechanical destruction such as dry, wet, and vibratory ball mill, wet ball mill with simultaneous saccharification processes, compression milling and other types of milling are pretreatment technologies that require long time, large energy and expensive equipment [31]. According to research conducted by Licari [31], namely pretreatment using a vibratory ball mill with a frequency of 15 Hz for 3 hours on sugarcane bagasse as a raw material to produce biomass with a Crystallinity Index (CrI) of 2.5% from the previous 64.5% while the sugar yield after enzymatic hydrolysis was 95.2%. (375mg / g biomass). However, when viewed from the perspective of energy use, an efficiency of 0.015 kg glucose / kWh of energy required for pretreatment is obtained. Energy consumption in the milling process will increase significantly with smaller biomass particles [64]. From a sustainable technology perspective, it is very important to determine the desired particle size for enzymatic processes. For certain applications such as molecular extraction, higher energies for the milling process are acceptable. However, for the conversion of biomass to energy, pretreatment energy must be kept as small as possible in order to be cost effective. However, with a small amount of energy, the resulting particles will be larger, thereby reducing glucose yield during enzymatic hydrolysis. Apart from energy reasons, this pretreatment method is ineffective for hard biomass such as empty palm fruit bunches. According to research conducted by Zakaria [32], namely pretreatment using a ball mill with a speed of 250 rpm for 2 hours on raw material for empty palm fruit bunches to produce biomass with a Crystallinity Index (CrI) of 9.3% from 56.1% previously while the sugar yield after enzymatic hydrolysis was 62.4% (393.6mg / g biomass). The yield of glucose from oil palm bunches is less than that of sugarcane bagasse.

6.2. AFEX pretreatment
Ammonia Fiber Explosion is an effective pretreatment method for soft biomass materials from agricultural waste, but not for hard biomass materials. Research using the AFEX method applied to soft biomass such as sugarcane bagasse, waste harvest corn and rice straw. Experiments by Gollapalli [33] with operating conditions at 90°C, 60% moisture content, and 2:1 ammonia ratio yielded 80% glucose and 80% xylose yield. Yield was not as expected for commercialization, namely 90%. Another experiment by Sundaram [34] with higher pressure operating conditions can produce glucose with a yield of 93% but the yield of xylose drops to 48%. This shows that the hemicellulose is degraded a lot into inhibitors thereby reducing the yield of xylose. Pretreatment was also carried out on the raw material for oil palm empty bunches by Lau [35] resulting in a yield of 58% glucose and 66% xylose. The AFEX method has been tested on a pilot scale using a reactor with a volume of 450 liters with yields of glucose and xylose greater than 19% and 15% compared to the results on a lab scale.

6.3. Ozonolysis pretreatment
Pretreatment using chemicals such as EDTA, ethylenediamin, dimethylsulfoxide, H₂O₂, KMnO₄, Na₂SO₄, and ozone are generally ineffective and too expensive in terms of cost. There has never been a
pilot scale study using this method. This was proven by Travaini [36] by pretreatment of sugarcane bagasse with an ozone flowrate of 60 L/hour for 45-195 minutes. The yield of glucose was 41.7% and xylose was 52.44%. In another experiment by Mardawati [65], the effect of ozonolysis on lignin degradation was 42.42%. Generally, effective pretreatment will produce degradation products that can inhibit the fermentation process. This is the biggest challenge in bioethanol production from lignocellulosic raw materials because inhibitors can block fermentation so that a detoxification stage is required which requires high costs. While the ozonolysis process specifically destroys lignin and does not produce derivative products such as furfural, HMF and phenolic components, it still produces derivative products in the form of organic acids [66].

6.4. Irradiation pretreatment

Pretreatment by means of irradiation consists of various types, including microwave, ultrasound, Gamma Ray, electron beam. This type of pretreatment is generally ineffective, slow, specific for certain biomass, requires high energy, and high capital costs in making tools. Experiments conducted by Diaz [37] with the microwave method at operating conditions of frequency of 2450 MHz and temperature of 180°C for 2 minutes on raw materials for harvesting corn and rice husks waste showed that microwave only degraded hemicellulose and did not show any effect on lignin and cellulose. For corn harvest waste raw materials, the yields produced were 24.1% and 17.2% for glucose and xylose respectively. In the raw material for rice husks, the yields produced were 4.2% and 1.9% for glucose and xylose respectively. The low yield obtained from pretreatment by microwave was obtained due to the lack of pretreatment intensity [37]. Another more intensive experiment on the same raw material was carried out by Wang [38] with an operating condition of 800 W microwave power for 5 minutes resulting in a glucose yield of 22.8% but there was degradation in lignin and hemicellulose. Low yields were also obtained at pretreatment using the ultrasound method by Wang [38] with sonication at a frequency of 40 kHz and a temperature of 80°C for 30 minutes resulting in a glucose yield of 17.8%. Low yields were also seen in experiments with other irradiation methods such as gamma ray ([67]; [68]; [69]) and electron beam [70]. Even though the irradiation method is not effective in pretreatment, it can increase yield when combined with other pretreatments [38].

6.5. Acid hydrolysis pretreatment

Various types of acid pretreatment have been found, such as using sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, and paracetic acid. Acid pretreatment with the addition of steam and steam explosion has also recently been studied. Various kinds of raw materials including timber, biomass with soft stems, herbal plants, agricultural waste, and waste paper are more studied, this is due to their low cost and effectiveness. The potential difficulty experienced now is the need for materials that are resistant to corrosion in reactors and the formation of gypsum, where sulfuric acid is being used incessantly due to the long-term prospects of chemical pretreatment. However, according to Pedroso [71] by conducting chemical pretreatment with various kinds of solvents such as H3PO4, H2SO4, HNO3, and HCL were obtained if the best pretreatment was found in H3PO4 solvent using rice husk as raw material. The yield concentrations of sugar produced in acid pretreatment with H3PO4, H2SO4, HNO3, and HCL solvents were 21%, 18.2%, 17.8%, 16.1%, and 17.8%, respectively. From this value, it can be seen that the resulting yield is small, this is due to the relatively fast pretreatment time of 28-60 minutes. By using other raw materials, according to Arishit[72] by performing acid pretreatment using H3PO4 solvent on coconut coir biomass, a sugar concentration of 21.98% can be produced by pretreatment at 95-100°C, for 1 hour. The main advantage of acid pretreatment or steam explosion with acid catalysis is that it can produce significantly higher xylose than other pretreatments. Using acid pretreatment with a batch system showed that the xylose yield reached 80% of the theory. Torget and Hsu [39], using two temperatures in acid pretreatment using a filtering process obtained yields of up to 90%. With steam explosion using an acid catalyst the yield was 90% from the literature. Even according to Zu [40] by using acid pretreatment with 1% HCl solvent with a temperature range of 100 - 130°C with a time of 20 - 40 minutes, the xylose yield was 97% using corn dregs as raw material. In addition,
there is research by Sindhu [41] using 3% sulfuric acid with a pretreatment time of 60 minutes, by varying the enzyme loading and incubation time, the yield of reducing sugar is 68.5%. And in the latest research, according to Rambo [42] using H_2SO_4 solution using raw materials in the form of coconut husk can produce sugar yields of 58.1% with variations in operating time and temperature.

### 6.6. Alkaline hydrolysis pretreatment

There are several studies that discuss alkaline pretreatment and mostly use sodium hydroxide solvents, or NaOH with a combination of other materials such as peroxides or other materials. If NaOH using or without soda ash is the best choice in terms of cost. Ammonia in liquid form was very effective in digesting solid residues but ethylene diamine solution was more effective. Yoon, et al. [73] used liquid ammonia by filtering, suggesting that the digestibility of poplar wood species is more effective. Steam explosion with lye in the research of Puri, et al. [74] suggested that the combination of a steam explosion with an alkali is more effective than a steam explosion without an alkali, or an alkaline alone without a steam explosion. The alkaline process is basically a delignification process [75]. In general, it significantly dissolves the whole hemicellulose. The effectiveness of the alkaline pretreatment varies widely, depending on external factors such as operating conditions and biomass used. The alkaline pretreatment is more effective at working on agricultural waste than biomass in the form of wood. By comparison with acid pretreatment, the need for a reactor is not like an acid reactor which must have resistance to corrosive properties, but in terms of pretreatment raw materials the cost is more expensive. Such as caustic soda is 4 times more expensive than sulfuric acid, and the base concentration is greater than that of acids. As according to Wu [43] using NaOH solution with a concentration of 1 - 5 M with a reaction time of 16 hours can only produce glucan yield of 85% using bagasse biomass as raw material. However, in Vaithanaomsat [45] research using coconut fiber as raw material can produce glucose levels of 45.59%. In the latest research, according to Rambo [42], with the same research as previously discussed, using 4% NaOH solvent using temperature and time variables, the highest sugar yield was 70.1% of these results, with the same raw materials, conditions. the same operation and different types of pretreatment then base has better results than acid pretreatment. According to Sangian [9] using coconut husk and NaOH solvent obtained sugar yield of 27%. Using 5% NaOH, the yield of reducing sugar was 22.89%. According to Liu [44], by using corn dregs raw material using the NaOH pretreatment method, at a temperature of 99°C for 1 hour, the yield of reducing sugar was 78.31%. By far, alkaline pretreatment is the most effective pretreatment for hard lignocellulosic biomass raw materials such as coconut husk and empty palm fruit bunches.

### 6.7. Organosolvent pretreatment

Using organic materials as solvents such as methanol, ethanol, acetone to dissolve and remove lignin (or so-called organosolvent processes) has been carried out in several studies. Organosolv processes with the help of acids or bases have also been carried out in several previous studies. The organosolv process itself is a process of delignification of hemicelluloses simultaneously. By using a catalyst, the process of hemicellulose dissolution is increased, and the digestibility of biomass is also increased. But the organosolv process itself is quite expensive in terms of raw materials and equipment because it requires high pressure equipment and is a complex process [16]. In some recent studies, ionic liquid (IL) has been used as a new type of solvent and a more environmentally friendly technology developed from organosolv. This is based on the use of IL as an organic solvent with recoverable properties. But behind the technological advances in the presence of this IL, there are several challenges behind it, including the high cost of IL, the need for regeneration, toxicological data, and the characteristics of IL in dissolving lignin and hemicellulose whether other inhibitors are formed or not. The functions and uses of IL are the same as that of organosolvents, namely to break lignin and hemicellulose bonds and reduce cellulose crystallinity. According to An [46] using IL in the form of cholinium argininate at 90°C for 12 hours, the glucose yield in rice stalks was 21.2%, rice husk was 25.8%, and bagasse was 20%. From the results of the pretreatment, it can be recovered 8 times with the last recovery result of 95.5%. In terms of the structure of this IL pretreatment from research it can make the structure more amorphous and
crystalline, there is structural damage, especially in lignin and hemicellulose. From the research by Nguyen [47] by pretreatment at 130°C for 24 hours, the glucose yield was 97% and the IL was recovered by 20 times and the yield value in the last recovery was 78%. According to Yoon [48] by conducting IL pretreatment on bagasse at 145°C for 15 can produce a reduced sugar yield of 69.7%, and in terms of structure on bagasse biomass according to Nasipour [76] pretreatment carried out at 130°C for 90 minutes can increase cellulose levels from 44.84% to 79.7%, decreased hemicellulose levels from 31.25% to 2.95% and lignin levels from 23.9% to 17.35% and the crystallinity index (CrI) from 0.28 to 0.073. Furthermore, the pretreatment process carried out on empty oil palm bunches according to Katinonkul [49] can remove lignin by 52.6%.

6.8. Liquid hot water pretreatment
The liquid hot water (LHW) method, also called the hydrothermal method, is a pretreatment by bringing the biomass into contact with high temperature water. This method has long been used since more than a century ago [77] but its designation is not for biofuel production. LHW pretreatment has been widely used because of several advantages, namely environmentally friendly, low cost, no addition of chemicals, and the potential for utilization of hemicellulose degradation products [78]. In the LHW pretreatment, organic acids are formed from degraded hemicellulose and causes hydrolysis of cellulose, especially at high temperatures (> 170 °C) [79]. This pretreatment has also proven effective in increasing the results of enzymatic hydrolysis of corn harvest waste and insoluble cellulose (solid phase) can be hydrolyzed effectively after the pretreatment process. Even though hemicellulose and cellulose are degraded, only part of the lignin content in the biomass is degraded and there is a change in the structure of lignin in the biomass [80]. Lignin is a binding agent in plant cell walls that holds cellulose and hemicellulose together. In addition to covering cellulose to be accessed by enzymes, lignin also binds cellulase so that less cellulase is available to access cellulose. Ko, et al. [80] reported that LHW pretreatment can destroy the structure of lignin so that lignin cannot adsorb enzymes. Experiments by Lu, et al. [50] with a condition of severity 3.9 in maize harvest waste showed 52.54% degradation of lignin and 98.62% degradation of hemicellulose so that it increased the cellulose content to 59.72% but there was also cellulose degradation of 21.9%. In general, the LHW process shows weakness in the form of low yield compared to other pretreatments due to hemicellulose degradation [51].

6.9. Steam explosion pretreatment
The pretreatment process using steam can be a steam explosion and wet-heat expansion. According to Saddler, et al. [81] Steam Explosion is one of the few pretreatment technologies that have evolved to the point that pilot scale and process equipment are commercially available. However, many research reports that steam explosion produces small xylose yields (not more than 65%). This is a major barrier to making the steam explosion method doubtful for ethanol production. The chemical process that occurs in the steam explosion pretreatment is that the high temperature of the steam causes the release of organic acid functional groups from the biomass and becomes a catalyst for the hydrolysis process. This process is referred to as the autohydrolysis process in the literature. The advantages of the steam explosion method are that there is no use of chemicals so that the cost is cheaper and the moisture content is low, causing less energy requirements. The effect of steam explosion pretreatment will be the same as pretreatment with acid but the less moisture content causes the resulting product not to be in the form of a slurry. Steam explosion is the most widely used chemical-physical pretreatment method for lignocellulosic biomass. Steam explosion is a hydrothermal pretreatment by contacting the pressurized steam on biomass for a few seconds to several minutes, then immediately lowering the pressure. This pretreatment combines mechanical forces and chemical effects due to autohydrolysis of acetyl groups released from hemicellulose. Autohydrolysis occurs due to high temperatures causing acid to form from acetyl groups and the result of water dissociation. The mechanical effect is caused by the pressure being immediately reduced and the fibers in the biomass being separated due to a sudden drop in pressure. Overall, the effects of a steam explosion are partial hydrolysis of hemicellulose, partial dissolution of hemicellulose, and redistribution of lignin structure and partial decomposition of lignin in biomass [82].
The loss of the hemicellulose surface makes the cellulose microfibrils more accessible to enzymes. The most important factors affecting the success of steam explosion pretreatment are the size of the biomass particles, operating temperature, residence time and the combined effect of temperature and residence time which is called the severity factor [83]. The higher temperature causes more hemicellulose to dissolve and hydrolyze, making cellulose easier to process, but the side effect is more sugar degradation products. Steam Explosion provides several advantages such as environmentally friendly, lower capital investment, more potential for energy efficiency, no use of chemical processes and hazardous conditions, and maximum sugar recovery [84]. Among its main advantages, other advantages are being able to use a large chunk of biomass, no need to add an acid catalyst, high sugar recovery, high results of enzymatic hydrolysis, and feasible application on an industrial scale. It should be noted that to obtain small pieces of biomass before pretreatment requires energy one third of the total energy required for pretreatment [23]. Although it has been said that adding acid is not necessary, if this is done, the sugar yield can increase without increasing the temperature so that the formation of degradation products can be reduced [85]. However, there are studies that the addition of acid causes an increase in equipment costs because it requires corrosion-resistant materials and from a process perspective causes the formation of more degradation products ([22]; [21]). Because low costs and low energy use are prerequisites for effective pretreatment, large particle size (before pretreatment) and the absence of added acid are desirable ways to obtain an effective pretreatment process [23]. Steam explosion technology has been proven to be used for ethanol production in a variety of raw materials such as cotton [86], olive waste [87], corn crop waste [88], and straw wheat [89]. This pretreatment process has given good results for hard raw materials and agricultural waste, but this pretreatment is not effective for soft wood because of the low acetyl group content in the hemicellulose structure [85]. Although it has many advantages and is feasible to be developed into an industrial process, the steam explosion pretreatment method has a major drawback, which is partially degrades hemicellulose to form degradation products that can affect the process of enzymatic hydrolysis and fermentation [86]. The amount of degradation product produced depends on the biomass feedstock used and the harsh operating conditions [21]. Various pretreatment studies on several tropical plant waste raw materials have been carried out using the steam explosion method. Wood [53] in a steam explosion pretreatment experiment with a temperature of 220 °C for 10 minutes on rice straw and rice husks, the results were 97.7% and 71% glucose yield, respectively. As well as reducing sugars, there are also derivative products of formic acid, acetic acid, 5-HMF and 2-furfuraldehyde which are respectively 14.3, 8.7, 1.07, and 0.78 g / kg of biomass in raw materials for rice straw and 6.9, 11.1, 2.6, and 2.7 g / kg of biomass in raw materials for rice husks. The experiment was also carried out with sugar cane bagasse by Dekker and Wallis [54] with a temperature of 200 °C for 10 minutes, then washing it to remove the inhibitor and resulting in a glucose conversion of 96.4% and a total sugar conversion of 89.3%. Steam explosion pretreatment in corn harvest waste with pressure variations of 1.5 - 3.5 MPa for 10 - 90 seconds resulted in the highest glucose conversion of 93.26% [55]. However, according to research by Bensa [56], steam explosion pretreatment on coconut coir with a temperature of 195 °C with a time of 10 minutes resulted in a lower glucose yield, namely 37.8%. This also happened to the raw material for empty palm fruit bunches which were pretreated at a temperature of 195 °C for 6 minutes and resulted in a glucose yield of 33.7% [90]. However, when an experiment was conducted on a pilot scale by Duangwang [57], pretreatment of empty palm fruit bunches resulted in a higher yield, namely 47%. Although the conversion yields of coconut coir and empty palm fruit bunches are low, steam explosion pretreatment provides by-products that are valuable. The steam explosion pretreatment process separates lignin by redistributing the lignin structure, not delignification or lignin degradation so that the lignin content can be recovered to become a by-product such as Lignin Plastic Composite Material (LPCM) and has been applied on an industrial scale with corn harvest waste as raw material. Purified hemicellulose degradation products can also add significant economic value.
6.10. Supercritical CO₂ pretreatment

Pretreatment explosion using CO₂ has been widely used either using steam or not using steam. According to Puri and Mamers [74], pretreatment using supercritical CO₂ is very effective, but this type of pretreatment is very ineffective compared to AFEX. This type of pretreatment itself has not had a pilot scale experiment. According to Huisheng [58] by conducting a CO₂ pretreatment process using corn dregs as raw material, with operating conditions of 11-19 MPa pressure, 100-180°C temperature, and 0-2 hours time, the glucose yield is 77.8%. According to Narayanaswamy [59] using the same material but with operating conditions of 3500 psi pressure, 80 - 150 °C temperature and 1 hour of time, the glucose yield is only 30%. In another study by Hamzah [60] using palm oil raw materials with a moisture content of 75% operating conditions, a pressure of 250 bar and a temperature of 130oC, a glucose yield of 24% was obtained. And according to Santos [61] by using palm oil raw materials with operating conditions of 12-16 MPa pressure and 60oC temperature obtained a glucose yield of 72%.

6.11. Biological pretreatment

In this pretreatment process that applies microorganisms that can dissolve lignin so that lignocellulose is formed which makes it easier for the enzyme to work. This type of biological pretreatment has the advantage of not requiring chemicals (if nutrients are not considered) and requiring little energy. So that this process can be considered environmentally friendly and energy efficient. However, this biological pretreatment process has the drawback that this process takes a long time and some microorganisms that dissolve lignin also consume hemicellulose and cellulose as well [20]. Therefore, this biological pretreatment has challenges from an economic point of view, and until now there is no pretreatment process that exists on an industrial or pilot scale, only on a lab scale. According to Wang [62], by conducting biological pretreatment using corn dregs raw material with the pretreatment method using peroxidase enzyme assistance with agitation 0 - 150 rpm, temperature 37-45 °C and enzyme incubation time for 48-72 hours, the yield value of sugar was 32.3%. In another study by Sun [63] on the same raw material and with the help of Trametes hirsute yj0 bacteria with an incubation time of 42 days, the sugar yield was 73.99%. In the same raw material, in a study by Saha [5] with the help of white-rot fungus with an incubation time of 30 days, a reduced sugar yield of 39.4% was obtained.

7. Conclusion

Based on the results of journal reviews and discussions, the following conclusions can be drawn based on the comparison between research methods, each pretreatment has its own advantages and disadvantages, but the most applicable pretreatment on an industrial scale is steam explosion for the following reasons: There is no need for a small size of pretreated biomass so that it is more energy efficient; No chemicals; Low water content results in energy saving; There is no degradation of cellulose and lignin so that the sugar yield is higher and lignin can be recovered; The degradation products of hemicellulose can be separated by washing and have economic value. Steam explosion is effective for soft lignocellulosic biomass raw materials but not effective for hard biomass such as coconut husk and cassava bunches. The best pretreatment for biomass raw materials is the alkaline method because alkalis are very effective in removing lignin and reducing crystallinity.

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