Valorization of Oil Palm Empty Fruit Bunch through Effectively Pretreatment and Hydrolysis of Lignocellulosic Biomass

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Abstract. Oil palm empty fruit bunch (OPEFB), a type of lignocellulosic biomass, is an easily obtainable resource for producing environmentally benign compounds like ethanol and levulinic acid. The difficulty of getting catalysts and enzymes to permeate the cellulose components in the biomass, however, is a major obstacle to turning it into useful compounds. Furthermore, because lignin is resistant, its presence may impede the conversion process. This work highlights different pretreatment strategies, such as lowering sugars and their derivatives, that are meant to improve the yield of important chemicals from oil palm biomass. In order to increase the effectiveness of the succeeding procedures that turn these materials into high-value compounds, a well-designed pretreatment technique is essential. The purpose of this research is to clarify the advantages and disadvantages of various pretreatment techniques used with oil palm biomass. It also examines how different pretreatment techniques affect the oil palm biomass's hydrolysis reaction efficiency.

Keywords: Biomass, Hydrolysis, Lignocellulosic, OPEFB, Pretreatment

1. Introduction

Despite being essential to the world economy, the palm oil sector has come under fire for its effects on the environment. One significant issue is handling empty palm oil fruit bunches, which are frequently thrown away as waste. These empty fruit bunches have a great deal of promise as important lignocellulosic biomass because they are leftovers from the palm oil
extraction process. To ensure the palm oil industry's sustainability and reduce its detrimental effects on the environment, research and development of efficient techniques for repurposing these discarded fruit bunches are crucial.

Oil palm trunks, empty fruit bunches (OPEFB), fronds, mesocarp fibers (OPMF), palm kernel shells (PKS), leaves, and shells are among the different types of biomass that come from oil palm trees [1,2]. Figure 1 lists the items made from oil palm plants along with some possible applications such as biofuels, fertilizers, animal feed, activated carbon, biodegradable material like bioplastic, etc. Thus, it is imperative to strategically increase the biomass's value across a range of applications, especially in order to address the energy problem and boost the economy.

![Fig. 1. Biomass wastes from oil palm tree. (modified of [3])](image)

The composition and structure of biomass vary based on its nature [4]. Typically, these differences arise from environmental factors, genetic influences, and their interactions [5]. Their physical characteristics and chemical makeup are where they differ most from one another. The majority of biomass wastes from oil palms have a high cellulose content. Similar to oil palm biomass, lignocellulosic biomass is composed cellulose and hemicellulose, which are essential components of conversion processes, as seen in Figure 2 shows mechanism of biomass conversion. Before high-value chemicals are produced, these components are typically converted into sugars and other intermediary molecules, such as furans.

Countless studies have explored various pretreatment methods for diverse lignocellulosic biomass types, yet none have comprehensively reviewed these methods concerning their efficacy in converting materials into value-added chemicals. This review paper evaluates all possible and current oil palm biomass pretreatment methods in an effort to close this gap. It will evaluate each method's efficacy according to the variables affecting the transformation into compounds with added value. The review will commence by providing an overview of the post-pretreatment composition of oil palm biomass, along with an analysis of the benefits and drawbacks of each pretreatment technique. It will also explore the ways in which these pretreatments influence the conversion reactions that follow. The novelty of this review is Enhanced Pretreatment Techniques: The study likely explores innovative or optimized pretreatment methods that efficiently break down the complex structure of OPEFB. This could involve novel approaches such as advanced chemical, physical, or biological methods that effectively disrupt the lignin-cellulose matrix.
2. Conversion of lignocellulosic biomass into value-added chemicals

Extensive research has been conducted on the transformation of agricultural byproducts, such as oil palm biomass, into valuable chemical compounds [6-16]. Producing energy-efficient biochemicals and biofuels from lignocellulosic biomass, such as oil palm biomass, is acknowledged as a vital approach to establishing a new economy that is not reliant on fossil fuels and reducing greenhouse gas emissions [7-17]. This biomass possesses significant potential for transformation into diverse compounds and intermediates. Some examples of valuable goods obtained from oil palm biomass are biofuels, such as biogas [8-18] and bioethanol [9-19], as well as acetic acid [10-20], formic acid [11-21], and levulinic acid [12-22]. Oil palm biomass is used to produce reducing sugars including sucrose, xylose, fructose, and glucose. Furthermore, the outcomes of furfural and hydroxymethylfurfural (HMF), significant biomass-derived intermediates, are presented. These intermediate compounds can undergo further processing to produce a range of molecules that contain an amino group, which are crucial for the pharmaceutical industry [13-23]. Improving the conversion of biomass and the selectivity of processes or technologies towards important platform molecules such as sugar, furfural, and 5-hydroxymethylfurfural is crucial for enhancing the conversion of biomass into valuable products [14-24]. Prior studies have demonstrated instances of valuable compounds obtained from oil palm biomass that are specifically designed for use in the biofuel, biogas, and biochemical sectors [15-19].

![Fig. 2. Production of levulinic acid and formic acid from biomass (Modified of Rackemann, et all 2014 [20])](image)

The process of transforming lignocellulosic biomass into compounds with increased value consists of three essential stages: pretreatment, hydrolysis, and fermentation [21]. Achieving
successful conversion hinges on an effective pretreatment, a crucial stage in optimizing the process. In its natural state, lignocellulosic materials are resistant due to the crystalline structure of cellulose and the presence of lignin. Lignocellulosic biomass consists of two main components: lignin and holocellulose. Holocellulose, in turn, includes cellulose and hemicellulose. The hydrolysis process is strongly affected by the length of carbohydrate chains, such as cellulose. Following the pretreatment process, cellulose and hemicellulose polymeric carbohydrates undergo hydrolysis more easily, resulting in the formation of free monomers such as glucose and xylose. Through the application of chemical or biotechnological methods, extensive research has been conducted on the conversion of glucose and xylose derived from lignocellulose into various chemical compounds and fuels.

Cellulose is a polysaccharide consisting of monomeric glucose units, joined by β-(1→4)-glycosidic linkages. It creates both highly organized and shapeless crystalline areas [22]. Cellulose, a key constituent of the plant cell wall, has distinct properties that enable the flow of nutrients and the preservation of cell shape due to its tensile strength [23]. The cellulose chain, which is a crucial component of carbohydrates, is characterized by its greater length, making it more difficult to break down through hydrolysis. The cellulose fibrils contain a crystalline structure that is held together by hydrogen bonds inside the structure. This gives the fibrils a natural ability to resist being broken down by biological or chemical processes [24].

Hemicellulose is a complex mixture of heteropolysaccharides found in biomass. It consists of branches of monosaccharide units such as pentoses (arabinose and xylose) and hexoses (galactose, glucose, and mannose). It forms non-covalent bonds with one or more cellulose fibrils and undergoes hydrolysis more easily than cellulose [25]. In the plant cell wall, hemicellulose interlinks with cellulose and lignin, contributing to the resistance of the cell wall [26]. Hemicellulose is classified into many types of cell-wall polysaccharides, such as xylan, galactan, xyloglucan, arabinan, and mannan. Enzymes catalyze the radical polymerization of three monomers: sinapy alcohol, p-coumaryl, and coniferyl alcohol. This process results in the formation of lignin, which is a three-dimensional amorphous phenolic macromolecule [27]. Lignin envelops and adheres to cellulose and hemicellulose [28]. To break down the lignin that is bound to hemicellulose compounds in order to obtain simple sugars and produce biofuels, the necessary steps for these compounds involve pretreatment, hydrolysis, and fermentation.

3. Pretreatment OPEFB

The high cellulose and hemicellulose content of oil palm biomass provides numerous advantages for the conversion of the biomass into valuable chemicals. Prior to initiating a hydrolysis reaction, it is necessary to subject the lignocellulosic biomass of oil palm, consisting of cellulose, hemicellulose, and lignin, to a comparable pretreatment in order to overcome the resistance of the biomass [29]. Pretreatments are used to increase the available surface area of raw materials by modifying their physical structures and chemical compositions before hydrolysis [30]. These pretreatments can disrupt lignocellulose crystallinity, remove lignin, increase biomass porosity, and reduce the degree of cellulose polymerization. From an economic standpoint, pretreatment holds immense importance, as subsequent processes like fermentation, downstream procedures, and enzymatic saccharification hinge on pretreatment outcomes. Various methods, including physical, chemical, physico-chemical, and biological pretreatments, can be applied to oil palm biomass to enhance the production of reducing sugars by mitigating barriers posed by lignin and hemicellulose.
3.1. Physical pretreatment

Physical pretreatment refers to techniques in which no outside materials—such as chemicals, water, or microbes—are used. Its main goal is to liberate intercellular components in order to decrease particle size, increase pore size, and improve surface area. This method seeks to accelerate the hydrolysis of cellulose and enhance the hydrolysis of hemicellulose. Physical pretreatment techniques are divided into three categories: mechanical, microwave, and ultrasound techniques [31]. However, a drawback of physical pretreatment is its high energy demand, rendering it economically unfeasible in certain cases. Consequently, numerous studies focus on finding more cost-effective methods. One recommended approach involves post-chemical pretreatment for size reduction, as it involves lower mechanical energy consumption [32].

In mechanical pretreatment, lignocellulosic materials are broken down to diameters between 0.2 and 2.0 mm using a range of processes such chipping, milling, and sieving to decrease their crystallinity [33-44].

The subsequent method involves the utilization of microwave radiation. The utilization of microwave irradiation in pretreatment has enabled several applications such as sterilization, cooking, microwave-assisted chemistry, drying, and heating. Present technologies propose utilizing a microwave-based approach for processing lignocellulosic materials [34]. By interacting molecules-to-molecules with an electromagnetic field, this technique transfers microwave energy straight to polysaccharides. However, because microwave radiation doesn't offer enough energy to start chemical processes, it can't produce effective material activities on its own. Consequently, in order to supply ions and polar molecules for this pretreatment and speed up both physical and chemical reactions, catalysts are needed [34]. The ultrasonic method is a comprehensive strategy. Ultrasound has been proven effective in improving the hydrolysis of cellulose, hemicellulose, and lignin, as well as totally eliminating cellulosic fiber from the paper [47]. Ultrasonication pretreatment enhances the biomass's surface area and alters its crystallinity, but it does not break down the biomass into sugars. Instead, it produces a preprocessed surface that is more readily susceptible to hydrolysis. Ultrasound pretreatment, conducted at a temperature of 50 degrees Celsius for a duration of 15 minutes, with a liquid-to-solid ratio of 10:1 (volume to weight), and a power level of 100%, when paired with Organosolv pretreatment using 30% ethanol, results in the production of 41.3 mg of reducing sugar [15].

3.2. Chemical pretreatment

Acids, alkalis, organic solvents, and ionic liquids are among the chemical treatment techniques that have shown to be quite successful in accelerating the breakdown of cellulose. By eliminating lignin and hemicellulose, decreasing the crystallinity of the biomass cellulosic constituents, and raising polymerization levels [48], they accomplish this. Among organic acids, catalysts such as oxalic acid, salicylic acid, and acetylsalicylic acid show promise. Aqueous organic solvent mixtures with inorganic acids like sulfuric acid (H2SO4) and hydrochloric acid (HCl) can also successfully disrupt internal hemicellulose and lignin linkages. However, because concentrated acid is corrosive, using it is not advised. This review's next section will examine many chemical pretreatments tailored to oil palm biomass. Pretreatments with acids and alkalis are among the standard procedures. Hemicelluloses and lignin are liberated from lignocellulosic material and distributed among the lignocellulosic fibers during the alkaline pretreatment procedure. Both the ester linkages in lignin and hemicelluloses can readily degrade under alkaline circumstances. Additionally, at elevated temperatures, the ether connections can also be disrupted. Notably, this breakdown
results in a substantial amount of cellulose being exposed to catalysts or enzymes as a result of the solubilization of hemicellulose and lignin [33].

Despite the potential cost reduction and energy consumption benefits associated with using biomass for fuels and chemical production, the use of acid in these processes comes with drawbacks like corrosion and pollution [35]. These issues have prompted researchers to seek alternatives for biomass pretreatment. Pretreatment using Ionic Liquids (ILs) has gained significant traction as these solvents are considered “designable” and environmentally friendly. This technology has attracted global attention, especially in industrial applications, because of its unique benefits such as low flammability, excellent chemical stability, broad electrochemical reactivity, strong ionic conductivity, little vapor pressure, and simplicity of recycling.

Katinonkul and colleagues [36] conducted a comparison among four classes of ionic liquids for pretreating OPEFB. The classes of chemicals used in the study were 1-ethyl-3-methyl imidazolium diethylphosphate ([Emim]DEP), 1-butyl-3-methyl imidazolium chloride ([Bmim]Cl), 1-ethyl-3-methyl imidazolium acetate ([Emim]OAc), and tributyl methyl ammonium methylsulfate (MTBS). The researchers found that [Emim]OAc, when used at a temperature of 110°C for 2 hours, achieved an impressive 96.6% enzymatic digestibility during the pretreatment of OPEFB. This particular ionic liquid was particularly effective in removing 52.6% of lignin, as well as reducing cellulose crystallinity and polymerization degree. In another experiment involving oil palm fronds, a 100% recovery of glucose was obtained within a 15-minute period at a temperature of 80°C with a solid loading of 10% [37].

Abu et al [38] delved into optimizing the conditions for extracting lignin from OPEFB using ([Bmim][Cl]) and a catalyst (H2SO4). They investigated various parameters such as the concentration of the catalyst and the ratio of ionic liquid to OPEFB. Their findings indicated that the optimal conditions for yielding lignin at 26.60% were achieved with a ratio of 3:1 wt/wt (ionic liquid to OPEFB) and a catalyst concentration of 4.73 wt%.

3.3. Combined chemical-physical pretreatment

Various studies have explored merging distinct pretreatment approaches for oil palm biomass, particularly by blending physical or mechanical treatments with chemical ones. Research indicates that combining chemical and mechanical methods for biomass preparation enhances the extraction of reducing sugars and advances the delignification of biomass.

Like mentioned earlier, milling stands out as a physical pretreatment method offering unique benefits, whether conducted before or after chemical treatment. When chemical pretreatment precedes milling, it reduces energy consumption and simplifies the solid-liquid separation process, resulting in cost efficiency. For instance, the combined approach of superheated steam (hydrothermal pretreatment) and wet disk milling (WDM) for oil palm mesocarp fiber (OPMF) led to significantly improved glucose and xylose conversion yields compared to sole WDM pretreatment [39].

Julio-Altimiranda et al. [40-51] conducted research that combined physical pretreatment via milling with chemical treatment using urea. They found that the size of the articles had very little effect on the outcome when they were milled and sieved. The worst outcomes were shown with samples that were 2.0 mm in size. Significantly, the most significant discovery was a decrease in sugar recovery in samples that underwent pretreatment with urea concentrations of 4% and 6% w/v. The decrease in yield can be attributed to the destruction of the polymer structure in lignocellulose caused by urea, which disrupts the links between callose,
hemicellulose, and lignin. Furthermore, their research emphasized the superior effectiveness of oil palm empty fruit bunches (OPEFB) in comparison to palm kernel shells, mainly because of the reduced lignin content present in the OPEFB structure.

3.4. Biological pretreatment

The biological pretreatment process is based on the utilization of microorganisms such as bacteria and fungi, which employ their enzymatic properties to modify lignocellulose structures and degrade lignin. There are a number of benefits associated with this technology, such as a simple process, low energy and capital requirements, no chemical interaction, substrate selectivity, and mild environmental operation [49].

White rot fungi have significant potential in breaking down lignin through the application of lignin-degrading enzymes such as Laccase, Manganese Peroxide, and Lignin Peroxide. Risdianto et al. [41] investigated the efficacy of White Rot Fungi of Marasmius sp. on oil palm empty fruit bunches (OPEFB), finding that these fungi could dissolve up to 35.94% of the lignin. However, hemicellulose and cellulose content in the OPEFB remained relatively unchanged. Isroi et al. [49].

4. Lignocellulosic Biomass Hydrolysis

After pretreatment, the subsequent step is the hydrolysis of lignocellulosic biomass, which entails converting cellulose and hemicellulose into sugars usable in producing biofuels, bioplastics, and diverse chemicals. Hydrolysis methods encompass enzymatic, acidic, or alternative approaches. The careful selection and optimization of the hydrolysis method play pivotal roles in maximizing the value derived from empty fruit bunches as part of the effort to enhance their worth.

4.1. Acid hydrolysis

OPEFB biomass was subjected to acid hydrolysis in 125 ml Erlenmeyer flasks. The solution had a concentration of 2–6 g of H$_2$SO$_4$ per 100 g of liquid, maintaining a ratio of 1 g of OPEFB fiber to 8 g of liquid on a dry basis. This hydrolysis process took place at 120°C, with samples taken at various intervals ranging from 0 to 90 minutes. Following collection, the samples were diluted with water and filtered to remove any insoluble materials from the liquid. The levels of xylose, glucose, acetic acid, and furfural were then measured in the resultant filtrate.

The fiber derived from OPEFB, a byproduct of palm oil mills, contains approximately 24% xylan, a significant source of xylose. Acid hydrolysis trials were carried out on OPEFB fiber at 120°C, employing varying concentrations of H$_2$SO$_4$ (ranging from 2% to 6%) and reaction durations (ranging from 0 to 90 minutes). The resulting hydrolysate exhibited peak concentrations of 31.1g/l xylose, 4.1g/l glucose, 3.3g/l furfural, and 3.93g/l acetic acid. Kinetic parameters were calculated using mathematical models to predict xylose, glucose, furfural, and acetic acid concentrations, improving the hydrolysis process's optimization. The optimal situation at 120°C were identified as a 6% acid concentration and a 15-minute reaction duration, yielding hydrolysate containing 29.4g/l xylose, 2.34g/l glucose, 0.87g/l furfural, and 1.25g/l acetic acid. The obtained xylose could be further converted into xylitol through a bioconversion process. Effective utilization of OPEFB fiber not only tackles environmental pollution concerns but also generates a valuable product for the palm oil industry [42].
4.2. Enzymatic hydrolysis

Enzymatic hydrolysis of plant biomass takes place within a pH range of 4.8, typically occurring at temperatures between 45-50°C. Various enzymes such as cellulase, hemicellulase, xylanase, peroxidase, and laccase are employed for this process [43]. Cellulase specifically targets cellulose polymers, while endoglucanases break internal β-1, 4 glycosidic bonds within the cellulose chain [44]. In many northern countries, these biological enzymes play a pivotal role in converting various properties of plant biomass. However, the biological hydrolysis method incurs high costs due to the necessity of expensive substrates for microbe growth or enzyme production. Despite the expenses involved, this method demonstrates significant potential for achieving high levels of delignification or enzymatic breakdown, especially in softwood biokonversion processes, although it remains in the stage of commercialization [45]. Some product can be produced after process pretreatment and hydrolysis as shown in Table 1.

Table 1. High-value chemicals or products from OPEFB [46]

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Pretreatment Method</th>
<th>References</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPEFB</td>
<td>Chemical : NaOH (alkaline)</td>
<td>[15]</td>
<td>Ethanol</td>
</tr>
<tr>
<td>OPEFB</td>
<td>Mechanical : Autoclave (Steam Explosion)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPEFB</td>
<td>Physico-chemical : Ammonia fiber expansion</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>OPEFB</td>
<td>Biological : Fungal Chemical : Wet Oxidation (Oxidative Delignification)</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td>OPEFB</td>
<td>Chemical : NaOH (Alkaline), Concentrated phosphoric acid (Acid)</td>
<td>[18]</td>
<td>Methane</td>
</tr>
<tr>
<td>OPEFB</td>
<td>Chemical : Some types of, (Ionic liquid)</td>
<td>[19]</td>
<td>Levulinic acid</td>
</tr>
</tbody>
</table>

5. Conclusion

Supporting the sustainability of the palm oil business requires the valorization of empty palm oil fruit bunches through efficient pretreatment and lignocellulosic biomass hydrolysis. Developing more advanced pretreatment and hydrolysis technologies is essential to properly use the substantial lignocellulosic biomass potential of empty fruit bunches. In addition to economic benefits, this approach also has a positive impact on the environment, helping to reduce the environmental footprint of the palm oil industry. Through continuous research and innovation efforts, we can achieve sustainability goals while maximizing the utilization of empty palm oil fruit bunches as a valuable resource.
References


