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Biomass Fuel Quality Improvement Using Hydrogen Peroxide and Demineralized Water Pre-treatment and Torrefaction

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Abstract: Biomass is a neutral carbon-potential solid fuel and, hence, it is environmentally friendly. However, biomass is characteristically hygroscopic, has a high-moisture content, a low calorific value, low resistance to biological degradation, and several storage issues. Therefore, torrefaction has received much attention in the last decade from researchers to overcome the problem because it can potentially improve the quality of biomass for fuel. This study examined the biomass pre-treatment technique and torrefaction for producing high-quality solid fuel. The empty oil palm bunches (EFBs) were soaked in 10% wt, 18% wt, and 26% wt of acid peroxide solution and demineralized water for 15, 60, and 120 minutes, respectively. Next, the EFBs were torrefied at 300 °C for 60 minutes. The 18% wt acid peroxide solution pre-treatment for 120 minutes has shown the best result with an ash content of 3.94% wt, volatile matter of 32.42% wt, and fixed carbon of 64.08% wt. Furthermore, the 60-minute demineralized water pre-treatment achieved the best results, reducing the potassium content by 30% (from 1.650% wt. to 1.144% wt.) and the chlorination by 48% (from 0.031% wt. to 0.016% wt.). The quality of EFB after burning largely meets the standards set by SNI 8675:2018. It has a maximum density of 0.8 g/cm3, a maximum water content of 12% wt., a maximum ash content of 5% wt., and a volatile matter content of 80% wt.

Keywords: Empty fruit bunch; Indonesia; Ash removal; Hydrogen peroxide; Torrefaction

1. Introduction

Empty fruit bunches (EFB) are a solid waste product of palm oil processing that has the potential to become a source of renewable energy commonly used as co-firing material in coal-fired power plants[1,2]. The torrefaction method is often studied for its effectiveness in improving solid biomass's physical and chemical quality, as it facilitates the decomposition of lignocellulose, composed of hemicellulose, cellulose, and lignin[3]. Additionally, torrefaction can reduce moisture content due to its operating temperature being above the boiling point of water[4]. Torrefaction converts biomass into fuel through thermal processing at temperatures between 200-300°C under inert conditions and at 1 atmosphere of pressure for 15-60 minutes. This method effectively reduces the oxygen-to-carbon and hydrogen-to-carbon ratios[5].

One of the variables that influence the success of torrefaction is the pre-treatment stage, as this stage can reduce the content of impurities that affect the quality of the biomass[6]. Many studies related to the pretreatment process of biomass have been conducted by researchers[7]. The pretreatment applied to the raw material aims to improve product yield through decreasing volatile matter and ash in the product. Furthermore, it has a significant impact on the structural characteristics of solid products[8]. The application of a pretreatment stage followed by torrefaction resulted in an enhanced quality biomass solid biofuel[9].

Generally, pretreatment applied to biomass involves the use of acidic or alkaline solutions since both indicated advantageous for torrefaction[10]. Acid successfully breaks down cellulose and hemicellulose into monosugars, followed by the hydrolyzation using dilute acid of the ether bond that links mono-sugar units in a polymer chain which decomposes the polysaccharide into monomers[11]. While alkalis promote the splitting of ester bonds in lignin polymers causes decomposition mechanisms in biomass.

The study conducted by Tabish et al. revealed that the pretreatment by using acid solution effectively removed the ash content and increased the heating value of biomass while the base solution could reduce the ash percentage of biomass[12]. Other research also confirmed that acid and alkali pretreatment proved beneficial for torrefaction by decreasing volatile matter, increasing yield, calorific values, and fixed carbon of the product[9] as well as removing ash[13], and the troubling elements such as Na, Cl, K, Ca, Mg, and others[14]. Both mild and strong acid solutions also efficiently eliminated inorganic material to varying degrees[15]. Based on study done by Alayont et al., acidic and alkaline pretreatment before torrefaction gave the high energy value biochar and also enhanced the properties of both bio-oil and biochar product[7].

Dual pre-treatment involves soaking the biomass in an acid or base solution at specific concentrations and durations, then drying in an oven until a constant weight is achieved[16]. Soaking biomass in a peroxide acid solution aims to reduce inorganic components, which can impact the torrefaction process. Also, soaking in demineralized water lowers impurities or unwanted substances[17]. Based on dual pre-treatment research, the highest calorific value was obtained from soaking coffee grounds in an 18% hydrogen peroxide solution, yielding 30.33 MJ/kg, exceeding that of the torrefaction process without dual pre-treatment[18].

Even though, dual pre-treatment in biomass conversion, often used to enhance the efficiency of breaking down lignocellulosic material for biofuel production, but it comes with several limitations. It can significantly increase operational costs due to the need for more reagents, equipment, and energy, along with added equipment maintenance[19]. The integration of different methods also presents challenges, as optimizing conditions for both pre-treatment processes can be difficult, leading to compatibility issues.

Additionally, dual pre-treatment often results in the formation of inhibitory by-products, such as furfural and phenolics, which hinder microbial fermentation and require further detoxification steps[20]. Environmental and safety concerns arise due to the use of hazardous chemicals, which necessitate careful handling and disposal.

Furthermore, material losses can occur, particularly in the form of sugar degradation and over-processed lignin, reducing overall yield. Scalability is another concern, as methods that work efficiently in the lab may be difficult to scale to industrial levels, both in terms of process control and energy consumption. Addressing these challenges is crucial for making dual pre-treatment economically and technically feasible for large-scale biomass processing[21].

Some important factors in the solution pre-treatment are type of solvent, concentration, temperature and time, biomass type, and pH control[22,23]. However, there is still limited research on the effects of pre-treatment of biomass, especially empty palm oil fruit bunches, to increase biomass utility for solid fuel, making this an interesting area for further investigation. Therefore, this study was focused on the EFB using hydrogen peroxide solution and demineralized water. The result will provide data on the improvement of biomass technology, and it is expected that this process can reduce the mineral content, thereby producing the best calorific value.

2. Methods

2.1 Material and Equipment

The biomass used in this study was empty oil palm fruit bunches (EFB) collected from a local palm oil mill. EFBs were sun-dried until their weight was reduced to less than 10%. Then, they were crushed and sieved to a size of 60 mesh. Subsequently, the samples were further dried in an oven at 105°C until a constant weight was achieved to obtain dry samples. They were then stored in tightly sealed zip lock plastic bags.

Demineralized water (DW), hydrogen peroxide (H_2O_2), and isopropanol were purchased from the local market. Demineralized water was used in the experiments as pre-treatment material, washing medium, and to prepare hydrogen peroxide (H_2O_2) solutions for various concentrations of 10% wt. (H10), 18% wt. (H18), and 26% wt. (H26). Meanwhile, the isopropanol was used to absorb tar from the outlet vapor of tube furnace reactor.

This study employed a range of specialized equipment to facilitate the experimental processes, ensuring precision and reliability in data collection. The equipment used includes:

- Tube Horizontal Furnace (Carbolite GVA 12/600): This furnace operates at a maximum temperature of 1200°C and features a heated tube length of 600 mm. It is equipped with advanced temperature control mechanisms, achieving an accuracy of ± 1°C. The furnace is capable of functioning under vacuum or inert gas conditions, making it suitable for thermal treatment, gas flow reactions, and material testing.
- Muffle Furnace (Vulcan D-556): This furnace also reaches a maximum temperature of 1200°C and is designed for open-air applications. It includes a digital temperature controller with an accuracy of ± 1°C, primarily used for ashing, heat treatment, and material testing processes.
- Oven (Memmert UN 110): With a chamber volume of

108 liters, this oven operates within a temperature range of +30°C to 300°C, offering a temperature accuracy of ± 0.3°C at 150°C. It is utilized for drying, heating, sterilization, material testing, and environmental simulation.

- XRF Analyzer (Xenemetrix): This instrument was employed for elemental analysis across a variety of sample types, including solids, powders, and liquids. It is capable of detecting elements ranging from sodium (Na) to uranium (U), providing comprehensive compositional data.
- Crusher (Xinyu Electric Motor BDCW): A powerful and efficient machine designed for size reduction of diverse materials, the BDCW crusher is commonly used in the mining and mineral processing sectors, as well as in construction, metallurgy, and chemical industries.
- Electric Sieve Shaker (JAG-375-B): This versatile tool is utilized for particle size analysis in both industrial and laboratory settings. It accommodates sieve diameters ranging from 200 mm to 300 mm, allowing for effective separation and classification of particles.
- Analytical Balance (Mettler Toledo ME204E): This precision weighing instrument features a maximum capacity of 210 grams and a readability of 0.1 mg, making it essential for accurate sample measurements in laboratory applications.
- Glass Laboratory Equipment: Various glass apparatus was utilized throughout the experiments to support sample handling and analysis.

2.2 Pre-Treatment

Sixty grams of the sample was placed into a beaker glass for soaking in H10, H18, and H26 solutions and DW. Additionally, variations in soaking time are conducted for 15 minutes, 60 minutes, and 120 minutes. The selection of hydrogen peroxide concentration variations and soaking time variations are based on the study by Chen and Martin respectively[18,24]. After soaking, the samples are dried in an oven at 80°C for 2 hours.

2.3 Torrefaction

Torrefaction is carried out under an inert atmosphere of 10 ml nitrogen per minute, reactor pressure of 1 atm, process temperature of 300°C, process duration of 60 minutes, and heating rate at 5°C/minutes. Purging before torrefaction is essential to ensure the absence of oxygen within the reactor. The main product obtained is charcoal, with a by-product of liquid tar and gas[25], which is dissolved in the isopropanol provided at the reactor's outlet.

2.4 Analysis and Observation

The samples were analyzed quantitatively and qualitatively. Quantitative testing of samples involves proximate analysis, hydrophobicity, and density. Proximate analysis is conducted on samples before soaking, after soaking, and after torrefaction, including measurements of ash ASTM E1755-01[26], moisture (moist.) ASTM E1756-08[27], volatile matter (VM) ASTM E872-82[28], and fixed carbon (FC) content. Meanwhile, Qualitative testing of samples consists of physical properties such as changes in the color of the samples before soaking, after soaking, and after torrefaction.

In addition, analysis of potassium was performed before and after soaking using X-Ray Fluorescence (XRF-Xenemetrix). The best sample from hydrogen peroxide soaking was chosen based on the parameters of the lowest ash content and the highest volatile matter. Meanwhile, the best sample from demineralized water immersion was chosen based on the parameters of the lowest potassium mineral content and ash content. The complete process of this study is illustrated in Fig. 1 as follows.

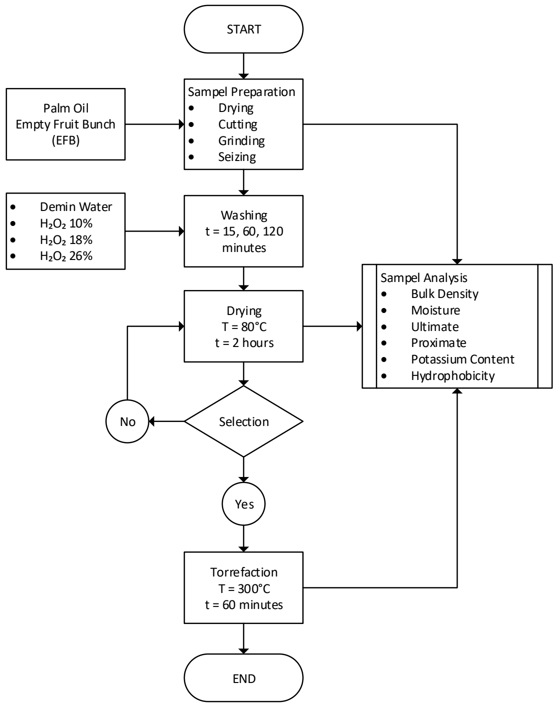

Fig. 1: Experimental Flowchart

3. Result and Discussion

3.1 Sample Characterization

Table 1 provides data on the composition of raw EFB in terms of ash, VM, FC, and moisture content in two conditions: "Dry Basis" and "As Received". A high percentage of volatile matter indicates a high energy content, making the EFB a good candidate for bioenergy production. The ash content can affect the efficiency of energy conversion processes and limit the use of high-temperature boilers. Moreover, the moisture content can influence the calorific values. The lower the moisture content, the higher the calorific values. It also causes the easiness of handling and processing of the EFB[29].

Table 1. Proximate Analysis of Raw EFB.

Proximate (% wt)	Ash	VM	FC	Moist.
Dry Basis	6.1	85.9	8.0	-
As Received	5.7	80.1	7.5	6.8

The moisture content of the dry basis EFB in this study was found to be 6.8% wt. A similar study by Novianti measured the moisture content of dry basis EFB of 31.2% wt.[30–32]. The difference in values is attributed to the additional drying steps in this study, which included sun drying and oven drying, resulting in a moisture content of less than 10%. Maximizing the reduction of biomass moisture content is crucial to making the biomass ideal for use as fuel, as high moisture content can hinder the combustion process.

3.2 The Effect of Soaking on Ash, Volatile Matter, and Fixed Carbon

Figure 2 depicts the analysis of volatile matter, ash, and fixed carbon content, respectively, for raw and pre-treated EFB. Soaking of EFB from 15 minutes decreases the volatile matter about 65 %, which the lowest volatile matter was achieved by using H18 following by H26, H10, and demineralized water respectively. Increasing soaking time of EFB tends to slightly rise the volatile matter about 1 or 2%. In the terms of ash content, increasing soaking time effects the decreasing linearly of ash in the EFB by using H10 and H18. The different trend was given by H26 and demineralized water. The highest ash content for H26 and the lowest ash content for demineralized water were identified at 60 minutes soaking time.

Later, the fixed carbon of EFB was range around 60% to 70% wt. It can be seen that H18 and H26 give high fixed carbon among of them. Hence, soaking of EFB using H18 for 120 minutes shows the optimal run based on the criteria of the lowest ash content, highest volatile matter, and highest fixed carbon. Hydrogen peroxide is an oxidizing agent containing free radical components and can enhance the decomposition of lignocellulosic compounds[33]. Hemicellulose is easily decomposed by alkaline or acidic solutions[34]. Cellulose can be de-crystallized by peroxide compounds[35].

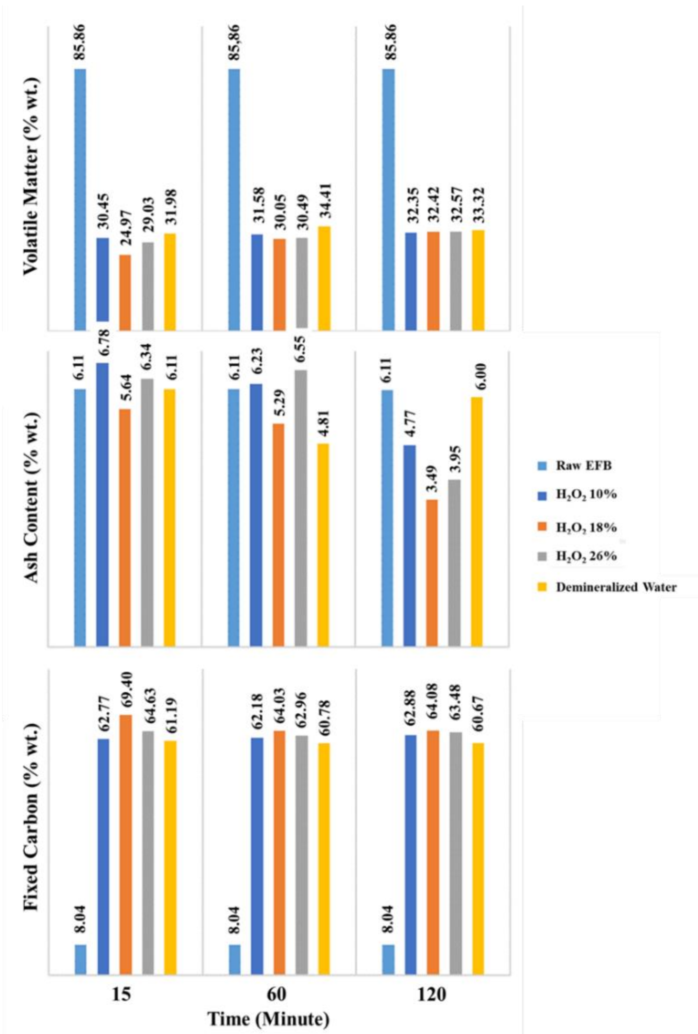

Fig. 2: Effect of soaking on the proximate part characterization: Volatile matter (top), ash (middle) and fixed carbon (bottom).

Additionally, the free radical components contained in hydrogen peroxide will react faster with lignin.

Considering that the initial treatment performed is a series of processes before torrefaction, it is necessary to note that in torrefaction, lignin compounds must be preserved because their carbon content is higher than that of cellulose and hemicellulose[36], which can improve the quality of biomass fuel. Based on the test results, EFB samples soaked in 26% hydrogen peroxide concentration (H26), whether for 15, 60, or 120 minutes, none of them exceeded the fixed carbon of the samples soaked in H18. The higher the concentration, the freer radicals it contains, thus enhancing the ability of hydrogen peroxide compounds to decompose lignocellulosic compounds contained in the sample.

Furthermore, soaking EFB in demineralized water has been shown to reduce ash levels at the 60-minute run. Most of the ash in biomass can be extracted through water washing[37]. Generally, the longer the soaking time, the more ash can dissolve. However, at the 120-minute run, the ash level is higher than at the 60-minute run. One of the contributing factors is saturation, which cannot dissolve more soluble substances. Accumulating ash on the heater surface and combustion area can lead to decreased combustion efficiency and increased risk of equipment damage. Therefore, with the initial treatment using demineralized water soaking, the ash content of EFB was successfully reduced. The highest volatile matter content aligns with the lowest ash content because the lowest ash content indicates that most of the minerals have dissolved in demineralized water. The remaining substances, or those not burned together with the volatile matter, are ash substances in which fixed carbon is contained. The fixed carbon represents the calorific energy a biomass can produce. The larger the fixed carbon, the greater the calorific energy that can be obtained

3.3 The Effect of Soaking on Sample Color

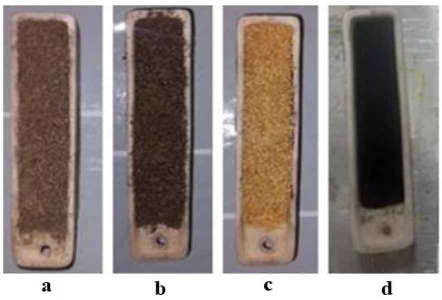

Fig. 3: EFB colors: a. fresh dried, b. DW soaking for 60 minutes, c. H18 soaking for 120 minutes, and d. torrefied.

The change in physical properties due to the color parameter of EFB can be observed in Fig.3. The results indicate that EFB is light brown on a dry basis (Fig. 3a). It becomes dark brown after soaking in demineralized water (Fig. 3b). After being soaked in hydrogen peroxide solution, it turns into a straw-yellow color (Fig. 3c). Finally, after torrefaction, it becomes a deep black color (Fig. 3d). It provides insights into how the color of EFB changes throughout the torrefaction process, which is crucial for understanding the thermal degradation and chemical transformations occurring within the biomass. Singh stated that the color shifting in torrefaction mostly caused by the changes in the acid-insoluble lignin component, rather than the carbohydrate portion[25]. These color changes reflect alterations in the composition and structure of the biomass, which can influence its suitability for various applications, including energy in thermal or electrical use and biofuel production.

There is a difference in the color of the EFB before and after torrefaction. Heat treatment of wood can cause color changes due to hemicellulose degradation[38]. Furthermore, other studies reveal that the color of EFB pellets changes to a darker or black after torrefaction[39,40]. Similarly, in this study, EFB, after torrefaction, becomes black for all sample variations.

3.4 The Effect of Torrefaction on Sample Density

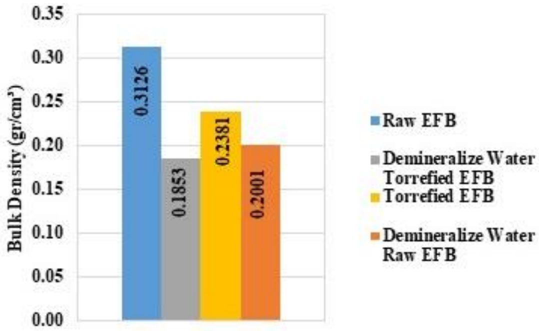

Fig. 4: Bulk Density.

Bulk density, commonly expressed in units of grams per cubic centimeter (g/cm^3) or kilograms per cubic meter (kg/m^3), represents the mass of a material per unit volume, accounting for the voids between particles[41,42]. It is determined by filling a container of known volume with dried material samples. The samples are lightly tapped to ensure settling without excessive compaction. The mass of the filled container is then measured, and the bulk density is calculated by subtracting the mass of the empty container from that of the filled container, then dividing the resulting mass by the volume of the container[42–44].

Based on Figure 4 above, the graphical trend indicates a decrease in density. This aligns with the findings of Yulianto, which stated that the torrefaction process of TKKS pellets results in a decrease in density values from 0.58 g/cm^3 to 0.48 g/cm^3 [45]. The disparity in density values is attributed to the difference in TKKS sample preparation, where in this study, a dry basis sample was utilized. Higher density implies greater resistance to combustion and a subsequent decrease in calorific value. Conversely, lower density facilitates oxygen diffusion through air voids and gaps in biomass, thus promoting combustion processes. Moreover, the particle size also related directly to the density[46].

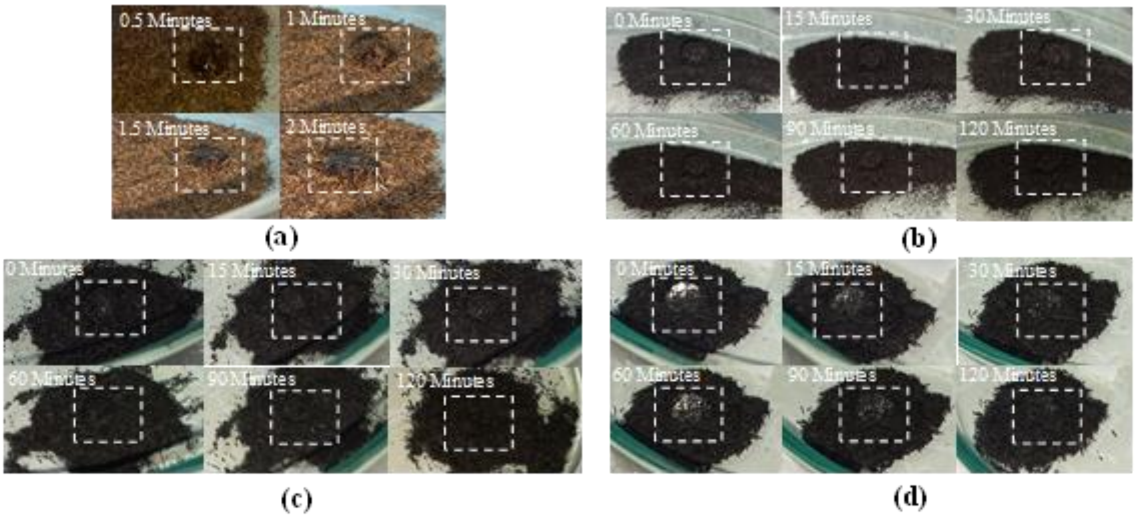

Fig. 5: Hydrophobicity test: (a) Raw EFB, (b) Torrefied EFB, (c) Soaked EFB in DM for 60 minutes, and (d) Soaked EFB in H18 for 120 minutes.

3.5 The Effect of Torrefaction on Sample Hydrophobicity

Torrefaction can reduce the hydrogen bonding of hydroxyl group of biomasses. It caused a decrease in moisture content, higher heating value, as well as increasing the microbial degradation resistance's[47–49]. Hydrophobicity describes the size of water contact angle formed by the material with a drop of liquid[50]. Normally, its range close to 90° or above for hydrophobic material[51]. The measurements aim to determine biomass's water absorption capacity. The absorbed water content will affect the effectiveness of combustion, making proper storage crucial, ideally in low humidity and sealed conditions. It can be measured by three method i. e equilibrium moisture content[52], contact angel[53–55], and water drop penetration[56]. Figure 5 shows the analysis of hydrophobicity using water drop penetration time of several samples. Figure 5(a) represents EFB before treatment, where it absorbed water within 2 minutes when given a drop of distilled water. It indicates that raw biomass has hygroscopic properties and easily absorbs water. On the other hand, Figures 5(b), 5(c), and 5(d) represent torrefied EFB samples where water droplets were not absorbed for the 120-minute test. They indicate that the samples are hydrophobic. The hydrophobicity of EFB torrefaction in this study increased by up to 60 times. Similar research was conducted by Hidayat using EFB pellet samples soaked in distilled water for 30 minutes, resulting in torrefied samples without any deformation[38]. This characteristic is particularly advantageous as it contributes to the stability of the biomass during storage and enhances its energy density, making it a more viable fuel option[57].

3.6 The Effect of Torrefaction on Ash, Volatile Matter, and Fixed Carbon

Figure 6 shows the effect of the torrefaction process on the proximate analysis parameter. Compared to raw EFB, the volatile matter contents are generally decreased. Moreover, the fixed carbon content and ash contents have significantly increased. The ash content in raw EFB is 6.1% and has increased in all torrefied samples. The rapid burning of the biomass can increase ash content and devolatilization of biomass[58]. The ash can potentially lead to fouling and slagging in the boiler. Therefore, it is important to reduce or remove it from fuel. The presence of oxide compounds influences this study's ash content increase, which remained after torrefaction.

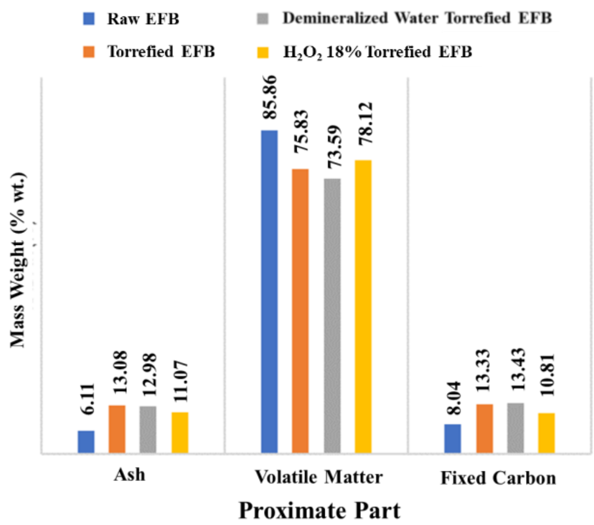

Fig. 6: Proximate analysis of torrefied samples.

Meanwhile, the volatile matter content of torrefied EFB has decreased from the raw biomass, ranging from 73-78 %wt. Since torrefaction only removed components in the biomass pores and the presence of rapid burning, thus the volatile matter content decreased, and the fixed carbon and ash content increased[58]. The increase in fixed carbon content enhances the calorific value of the biomass. Additionally, the analysis of fixed carbon content has shown an increase from 8.0 % wt. to 13.3 %wt. Higher fixed carbon content increases the calorific value of the solid products of torrefaction. With the increase in temperature during torrefaction, oil palm empty fruit bunch products exhibit better emission and hydrophobic properties.

3.7 The Effect of Torrefaction on Potassium

Biomass ash contains various elements and minerals, including potassium, contributing to fouling and slagging in boilers. Figure 7 shows potassium content in the fresh EFB ash after pre-treatment and post-torrefaction. The EFB samples soaked in demineralized water still contain potassium minerals as much 1.14 %wt, which had reduced 31% from its raw EFB. Other studies showed that the Potassium can be reduced as much as 50-97%wt[59].

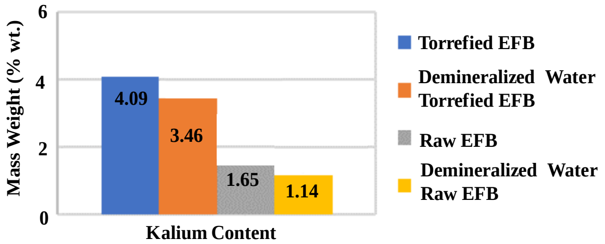

Fig. 7: Potassium content in ash.

The potassium was increasing in concentration after torrefaction. However, this increase is lower than in the torrefied samples without pre-treatment. It was because Potassium content is one of the mineral types present in EFB, known as ash-forming elements[60,61].

The ash-forming elements will be retained within the biomass during the torrefaction process, and their solid forms will remain as ash[62]. This retention of minerals like potassium leads to the formation of ash, which can be problematic in combustion systems. Ash accumulation can cause fouling and slagging in boilers, reducing efficiency and potentially damaging equipment.

The decreasing of potassium content was directly corelate with the increasing of washing time[63]. Therefore, to minimize the potassium content after torrefaction in EFB, maximizing the initial treatment stage of demineralized water soaking is necessary. It can be achieved by increasing the ratio of water to EFB and extending the soaking time so that more potassium is dissolved first. By ensuring that more potassium ions are removed during the soaking stage, fewer will remain bound to the EFB when entering the torrefaction stage. Consequently, ash formation can be minimized, reducing the negative impacts on combustion efficiency and equipment longevity.

4. Conclusion

Based on the research, soaking in demineralized water has decreased the potassium (K) content in EFB by 30.69%, respectively. Meanwhile, soaking with hydrogen peroxide showed an increase in mineral content. The best soaking result using demineralized water was for 60 minutes, as it resulted in the lowest mineral and ash content. On the other hand, the best soaking result using hydrogen peroxide was a concentration of 18% for 120 minutes, as it produced the lowest volatile matter and ash content. The soaking process has been shown to influence the chemical properties of the torrefaction products. Additionally, torrefaction has been proven to increase biomass hydrophobicity by 60 times. The torrefaction products have been shown to meet the SNI 8675:2018 standard, although further studies are needed to refine biomass quality for industrial use.

This study shows insight into increasing the potential use of empty oil palm bunches (EFB). However, several research limitations are identified, suggesting future research directions to enhance the understanding and application of biomass as a renewable fuel. Limitations include the narrow scope of pre-treatment variables, a single temperature and duration for torrefaction, and a focus on EFB alone. Additionally, the study needs comprehensive environmental and economic analyses and detailed post-torrefaction quality metrics.

Future research should optimize pre-treatment conditions, explore variable torrefaction parameters, and compare different biomass types. Long-term storage and degradation studies, detailed combustion characteristics, and economic and environmental impact assessments are essential. Integrating these processes into existing biomass supply chains, employing advanced analytical techniques, and conducting pilot-scale experiments and field trials can provide a deeper understanding and practical applicability of pre-treated and torrefied biomass. Addressing these aspects can significantly advance the use of biomass as an efficient and sustainable energy source.

Author Contribution

AA & PR are the research conceptor and design. PAN, SAA, BAF, DBIN, EFD, and HB contribute to the data collection and experiment. ARF, ERF, F, EWT, MS, I, and HS contribute to the data analysis and interpretation. PAN, SAA, AMN, MPH write the initial manuscript. AA, HS, UL, FY and PR perform the critical revision of the article. AA, MPH and PR ensure final approval of the article.

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