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Rice Husk Demineralization: Effect of Washing Solution on Its Physicochemical Structure and Thermal Degradation

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Abstract

Generally, biomass consists of various amounts of minerals. These minerals influence the biomass characteristics and behavior during their use in a thermochemical process such as pyrolysis. The conversion during pyrolysis and its final product will be affected. This research was carried out to study the impact of washing treatment in water and acid solutions on the rice husk as the raw material for pyrolysis. Also, the effect of acid strength (citric acid as the weak acid while nitric acid as the strong acid) and its concentration (1, 5, and 10 wt.%) was investigated. The results confirmed from the thermogravimetry (TGA/DTG) analysis, surface analysis (SEM), and spectra (FTIR) analysis describe the treatment using water caused less change on the rice husk surface structure and its thermal degradation. However, it seems hard to reduce the minerals (proved from XRF analysis). Meanwhile, the treatment using acids solution resulted in lower mineral composition than the rice husk without treatment. This result is more visible for demineralization using a 5 wt.% nitric acid solution. However, for a higher concentration (washing treatment using 10 wt.% solutions of nitric acid), the degradation on rice husk structure was more occurred.

1. Introduction

The decline of fossil fuel deposits is turning attention to find alternative energy for fossil fuel substitution. Biomass is one of the promising sources of renewable energy. Pyrolysis is a thermochemical decomposition of biomass results in fuel and/or chemicals at high temperature in the condition of oxygen absence. The important reasons should be evaluated for the effective design of pyrolysis reactor, not only on the source of biomass, operating conditions, and reactor configuration [1] but also on the minerals contained and their raw biomass composition [2]. In general, even at low content, these minerals, especially alkali and alkaline earth metals such as sodium, potassium, calcium, iron, and so forth, causes adverse effects such as accumulation of fouling on the surface of equipment, thus causes the overall rate of combustion decline [3, 4]. The physical and chemical properties of pyrolyzed oil resulting from the high mineral content of biomass can change easily during storage due to inorganic minerals. Minerals accelerate the polymerization reaction because it increases the viscosity of the pyrolysis oil [5].

Many researches have been conducted to remove the minerals from biomass. The most used method for removing the minerals is acid washing treatment. This method is effective in ash removal. Vamvuka *et al.* [4] used HCl, CH_3COOH, and HCl/HF solutions. Tan and Wang [6] found the order of mineral removal using acid solutions from white pine and rice husk was $HCl > H_2SO_4 > H_3PO_4$. They also stated that pyrolysis's bio-oil yield increased due to the increase in the HCl concentration from 3 to 7%. Numerous previous research studies have investigated the efficiency of various acid solutions during the washing process. Most of them studied the demineralization of various biomass using different acids at fixed concentrations [4, 6, 7, 8]. Meanwhile, Stefanidis *et al.* [9] studied the effect of strong and weak acid at low concentrations (up to 1 wt.%) and the effect of heating during demineralization. However, so far, only a few have reported the effect of different concentrations of strong and weak acid solutions during demineralization treatment on the biomass's physicochemistry. As reported in earlier research, acid treatments for biomass can significantly reduce minerals. However, at the same time, it was also probably washing away the acid-soluble components such as hemicellulose and cellulose [10]. This process can be observed through the change of physicochemical structure of biomass itself [5]. Therefore, this research was conducted to investigate the impacts of demineralization using water, nitric acid (strong acid), and citric acid (weak acid) at different concentrations of rice husk physicochemistry. Furthermore, the thermal degradation of treated rice husk was observed using thermogravimetric analysis (TGA). The weight decomposition of a sample for the temperature change is measured using TGA [11]. From the TGA curve and its derivative curve (DTG), the sample's weight loss with increasing temperature could be obtained [12].

2. Methodology

This study was conducted in three stages, including sample preparation, demineralization treatment, and sample analysis and characterization.

2.1. Sample Preparation

Rice husk was obtained from Gambut, district of Banjar, South of Kalimantan Province, Indonesia. It was ground and sieved to homogenize the particle powder to 18-60 mesh. Then the powder was put in an oven at 80°C for 3 hours to homogenize the sample's initial conditions before being used in the demineralization treatment.

2.2. Demineralization Treatments

In the washing process, the rice husk sample (20 g) was immersed in the washing solution (200 mL). This study's washing solutions were distilled water, citric acid solution, and nitric acid solution. The citric acid solution concentration was 1 and 5 wt.%, while a nitric acid solution was 1, 5, and 10 wt.% of concentrations. This solution was 300 rpm magnetically stirred at room temperature for 2 hours. Then it was filtered in vacuum condition. The acid solution samples were washed with distilled water to neutralize the pH. Finally, they were put in the oven at 80°C for 22 h and then placed in a desiccator for further analysis.

2.3. Sample Analysis and Characterization

The proximate analysis of the treated and untreated rice husk consists of moisture content, ash content, and the volatile matter was conducted according to ASTM D3173, ASTM E1755, and ASTM D3175. Then, the fixed carbon was computed by the difference. The morphology and surface structure of samples were studied by scanning electron microscopy (SEM) Inspect S50 at 12.5 kV and 1000 × magnification scale. The functional group's spectra were detected by Fourier Transform Infra-Red (FTIR) spectroscopy method using Thermo Scientific Nicolet iS10, observed in the range of 500-4000 cm^{-1}. The X-Ray Fluorescence (XRF) PANalytical/Minipal 4 was used to determine the samples' composition. Thermogravimetric analysis (TGA) was observed using a Thermogravimetry analyzer from Linseis STA PT 1600, with approximately 15 mg of a heated sample from room temperature to 600°C at a heating rate of 10°C/min under 50 mL/min of nitrogen flow.

3. Results and Discussion

The washing treatment was conducted to demineralize the rice husk sample as the pretreatment before being used as biofuel raw material via pyrolysis. This study found that the treatment changed the physical and chemical structure of the rice husk. Besides, it affected the thermal behavior of rice husk.

3.1. Physical and Chemical Characterization of Rice Husk

Proximate analysis for treated and untreated rice husk under free moisture conditions is presented in Figure 1.

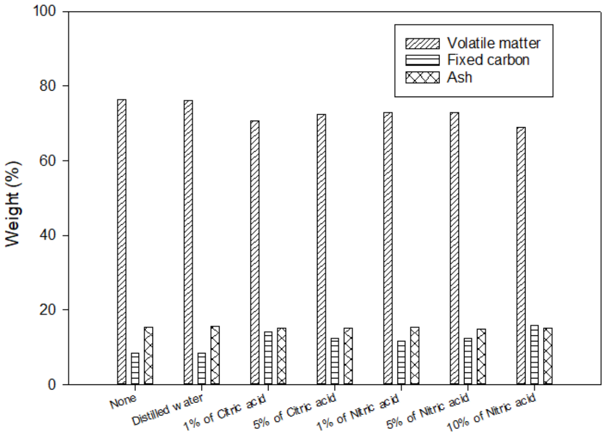

Figure 1. The proximate analysis results for untreated and treated rice husk (dry basis).

Figure 1 shows that washing treatment resulted in lower ash content and volatile matter while increasing the fixed carbon for all samples. After washing treatment, the minerals content declined proportionally with the acid's strength and its concentration (XRF results in Figure 4). The presence of minerals such as potassium (K) and calcium (Ca) promotes the gas and char formation but lowering the tar yield [13]. Also, Jiang *et al.* [14] concluded that the alkaline earth metal such as calcium (Ca) participated during secondary cracking of tar molecule and formation of gas-volatile. Thus, removing these minerals from the rice husk sample decreased volatile and ash content while the fixed carbon increased. However, the treatment in distilled water hardly increased the content of ash compared to untreated one, possibly due to the water-insoluble organics covering the surface [15] that is shown by white flake distribution that exhibited in Figure 2b SEM result. The ash removal after demineralization is calculated from the percentage of ash reduction compared to the untreated one. It was between 0.33 to 2.54%, and the highest removal was due to the washing in 5% of nitric acid solution. After demineralization, the low value of ash removal indicated that the ash in rice husk is not easy to remove. Raveendran *et al.* [16] also observed that the ash content in rice husk was hardly removed during demineralization. It could be because of the combination of high lignin composition with high potassium content (can be seen in Figure 4). The potassium content also explained why the volatile matter was increased due to demineralization, as this mineral influences the volatile formation [16]. Figure 1 also showed the highest removal was due to the washing in 5% nitric acid solution. It implies the minerals that significantly affect the ash content much easier to remove in the strong acid condition [6]. This result is consistent with the XRF results explained later.

The surface morphology of the rice husk can be seen in Figure 2. Untreated rice husk performs the regular stomata and epidermis clear surface (Figure 2a). The water washing treatment (Figure 2b) shows a similar surface as the untreated one, but with white flake distribution on the surface (supporting the ash content result). It was caused by the water-insoluble organics covering the surface [15]. Figure 2c to 2g present the surface of rice husk via acid washing treatment. Washing in acid solution in Figure 2c to 2g broke the rice husk's stomata, thus revealing a smooth epidermis [17]. This indicated acid washing treatment resulted in degradation on the rice husk surface. Furthermore, the degree of damage due to the washing was significant with the acid strength and concentration. As the acid strength and concentration rose, the surface degradation occurred (Figure 2g).

The transmission spectra of untreated and rice husk under washing treatment are shown in Figure 3. The peak of C-H at 2750-3000 cm^{-1} related to cellulose-rich functional groups. Whereas the peak of C=O as hemicellulose contribution presents at 1730 cm^{-1} [18]. Lignin functional groups were observed at 1600 cm^{-1} [19]. The peak of C-H of C-O at 1000-1100 cm^{-1} also contributed to cellulose [18]. The FTIR curves in Figure 3 show that cellulose and lignin functional groups for treated and untreated rice husk were not much different. However, it was a little change in hemicellulose and cellulose functional groups. The peak associated with cellulose at 1000-1100 cm^{-1} for untreated rice husk is quite clear. However, it seems only slightly decline upon the treatment with water and citric acid solution at low concentration (1 wt.%). However, this peak is almost not clear due to the treatment using a higher concentration of citric acid (5 wt.%) and nitric acid solution at any concentration. Moreover, the hemicellulose peak at around 1730 cm^{-1} for water and low concentration of citric acid (1 wt.%) is almost similar. However, there was a noticeable change in the shape of the peaks around the band, especially after treatment with higher concentrations of citric acid (5 wt.%) and nitric acid solution at any concentration. These results indicate that C=O bonds in hemicellulose and C-H of C-O bonds associated with cellulose are easier to break in an acid condition, especially at higher concentrations. This result supported the SEM and the TGA/DTG results later.

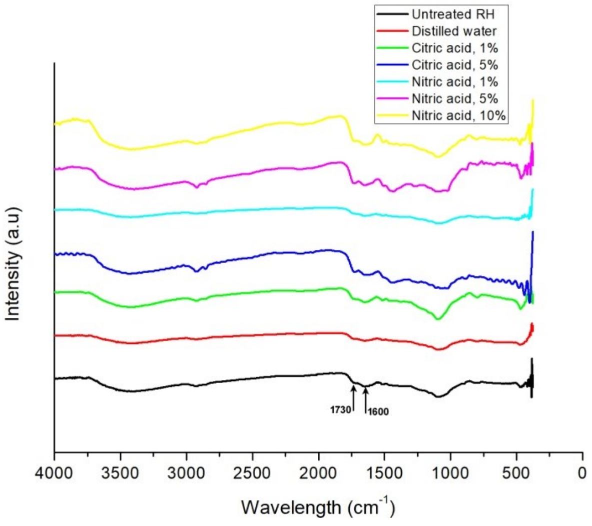

Figure 3. Rice husk FTIR spectra for various washing solutions

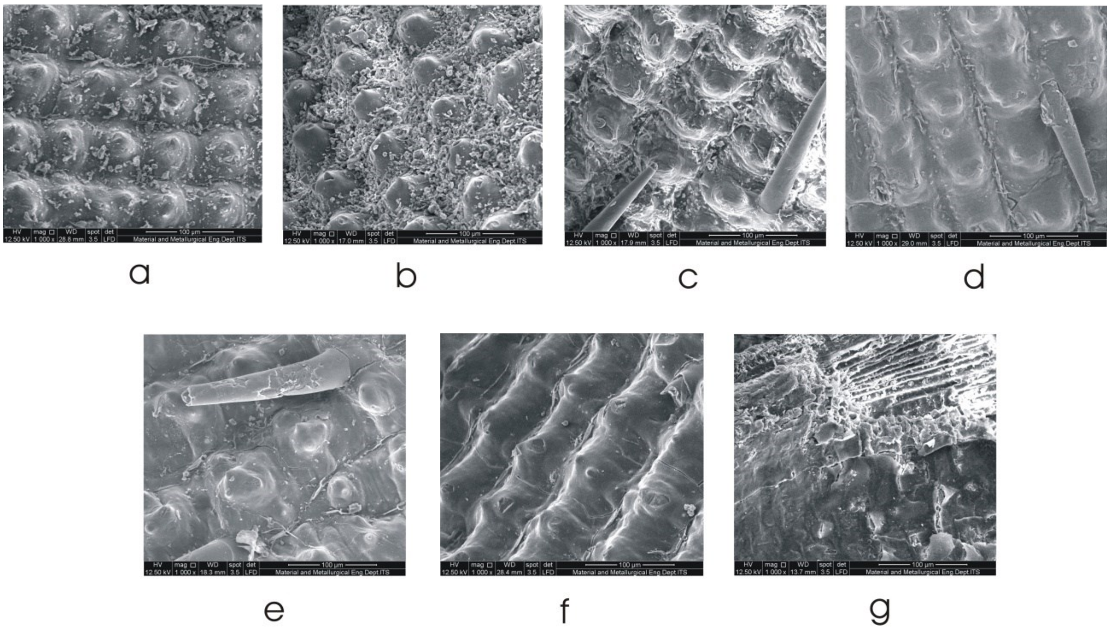

Figure 2. SEM images of rice husk (1000 x magnification) for (a) untreated, and treated by: (b) distilled water, (c) 1% citric acid, (d) 5% citric acid, (e) 1% nitric acid, (f) 5% nitric acid, (g) 10% nitric acid.

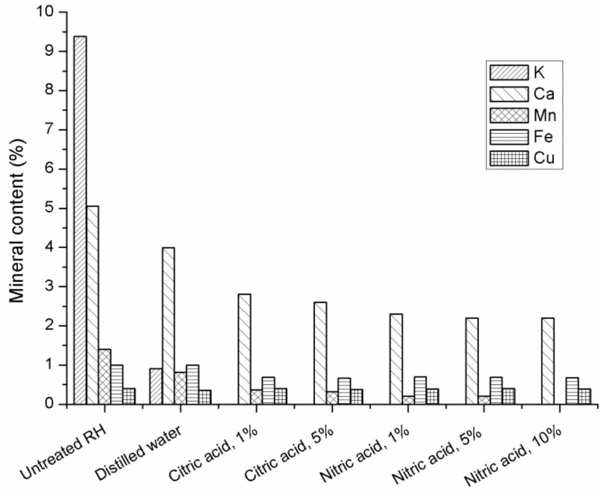

Figure 4. Mineral contents of untreated and treated rice husk.

The mineral contents resulted from the demineralization process are compared to the untreated one in Figure 4. Potassium (K) significantly decreased by about 90% upon the treatment with distilled water, while it was removed by acid treatment. However, the Calcium (Ca) reduction in distilled water was little, as observed by Shi *et al.* [20]. Calcium (Ca) was slightly decreased after washing by water. However, in acids, it further declined to 45-57% (from the lowest to the highest) in these orders, 1% of citric acid, 5% of citric acid, 1% of nitric acid, and 5% nitric acid, and 10% of nitric acid. Manganese (Mn) also performs similar behavior, but it is totally removed using 10% of nitric acid solution. Iron (Fe) did not appear to be affected by water leaching. However, it decreased slightly due to the acid washing, even though the reduction was constant at about 30% across all acid types and concentrations. The lower Fe content towards a constant value at acid leaching at any concentration indicates that the Fe in the rice husk sample is in the form of hematite which has high stability and is partly anhydrous [4]. Water and acid solutions had no significant effect on the Copper (Cu) content. Its content was almost the same for both treated and untreated ones. In other words, the ability to remove the minerals using water is lower than that of acids. Furthermore, the acid strength and composition will influence the decrease of mineral content as the lowest mineral content was obtained by washing with the nitric acid (strong acid) solution at a high concentration.

3.2. Thermal Degradation of Treated and Untreated Rice Husk

The TGA results in Figure 5 presents that the decomposition of the sample can be divided into four ranges: less than 100°C for water removal, followed by 200-350°C for hemicellulose decomposition. Then, cellulose decomposed at 350-400°C and greater than 400°C was lignin decomposition [21]. The range of water-washed and acid-washed TGA curves is not much different compared to the untreated one. However, the total solid residue at 600°C is different, proportional to the acid strength and its contents, which shows the lowest value for the treatment with 10% of nitric acid solution. This result implies the strong acid such as nitric acid at higher concentration resulted in the most dissolution effect to cellulose and hemicellulose compared to water and weak acid. This trend was also reported in [5]. Eom *et al.* [10] mentioned that the cellulose and hemicellulose of poplar wood were decreased upon the acid treatment. The reactivity of hemicellulose and cellulose was increased due to the removal of minerals [22]. It can be concluded that minerals in alkali metals contributed to the dominant role during decomposition. This result indicates that acid washing was lowering the thermal stability of rice husk [23]. It means rice husk's physical structure is much easier to decompose in acid conditions [24], especially at higher concentrations. Therefore, the total solid residue for each washing treatment at the end of TGA analysis temperature (600°C) is different.

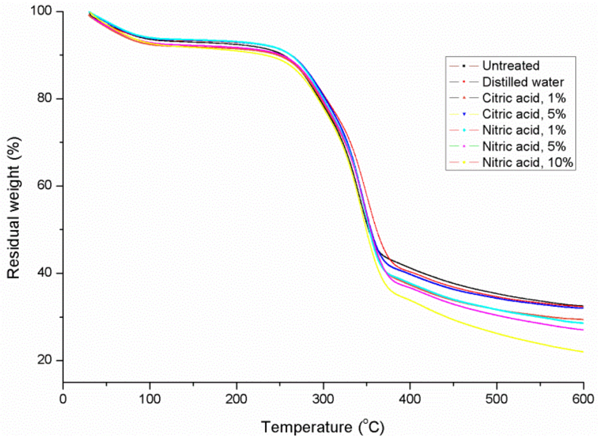

Figure 5. TGA plots of rice husk.

Figure 6 shows the DTG plots for the untreated and treated rice husk. The 1st and second peaks of the DTG curve for water and acid-washed rice husk were shifted to higher temperatures than the untreated one. The 1st peak, nearly 280°C, associates with the decomposition of hemicellulose, and the 2nd peak around 350°C indicated the cellulose decomposition was occurred [22].

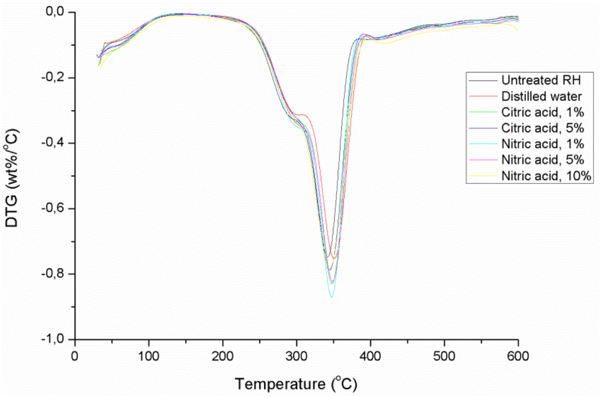

Figure 6. DTG plots of rice husk.

The maximum weight loss rate for the 1st peak varied at 0.314-0.359%/°C whereas the maximum degradation rate at the 2nd one raised to 0.748%/°C and 0.753%/°C for untreated and water-washed, respectively. In contrast, it increased to 0.787-0.870%/°C for acid-washed those in line with the acid's strength and concentration. The peak of the DTG curve indicates that the washing treatment makes the rice husks more thermochemically degraded. Also, the reactivity of hemicellulose and cellulose was increased due to the treatment [22]. From the rate of degradation, it can be concluded that cellulose was more active than hemicellulose upon the washing treatment. Moreover, the acid strength and its concentration are proportional to cellulose and hemicellulose reactivity, as observed by Ansharullah *et al.* [25]. They found the decrease of cellulose content significant to the HCl concentration increase used during the delignification process. However, it decreased at 10% of nitric acid to 0.782%/°C. Possibly the high concentration of nitric acid caused the structural change. This result implies that water and acids washing treatment reduced hemicellulose and cellulose left in the rice husk as dilute acid or base clearly hydrolyzes hemicellulose efficiently [10] (in agreement with FTIR and SEM results). Thus, washing treatment not only reduces the inorganic contents but also changes the biomass composition.

4. Conclusion

Acid solutions' strength and concentration influenced the degree of ash removal in rice husk upon the treatment. The minerals' content also experienced the same trends. They would decline as the acid became stronger as well as the acid concentration increased. This washing treatment also changed the biomass composition. The best result was achieved by using a 5% nitric acid solution. However, the treatment using 10% nitric acid solution results in the treatment effect declined, moreover the surface degradation was more occurred. This result implies that too high acid concentration will be an obstacle during demineralization.

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