Characterization of treated empty fruit bunches by thermogravimetric analysis (TGA)

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Abstract. This research investigates the thermal degradation characteristics of treated empty fruit bunches (EFB) using thermogravimetric analysis (TGA), contributing to circular economy promotion by encouraging the use of agricultural by-products in the energy sector. EFB feedstock was prepared by immersing 100g of residue in 1.8 liters of distilled water for 40 minutes at room temperature (~30°C). Results show that this treatment reduced ash content by approximately 2.74 wt%. TGA data reveals that untreated EFB exhibited greater weight loss compared to treated EFB, with the latter showing shifted decomposition processes at higher thermal degradation temperatures. The study explores ash's catalytic influence, providing insights into weight loss patterns and decomposition temperature ranges. This enhanced understanding of biomass behavior provides valuable data for optimizing biomass-based energy systems, further advancing sustainable energy solutions and resource efficiency.

1 Introduction

Biomass, in its diverse forms, is a key renewable energy source complementing diminishing fossil fuels. This versatile resource provides a clean, sustainable alternative for energy generation and high-value bioproducts. Converting biomass is both eco-friendly and economically viable, offering a sustainable solution to growing energy demands. Biomass-fired boilers face significant challenges with fouling, slagging, and agglomeration. These deposits on heating surfaces impair heat transfer efficiency. Severe buildup can force unscheduled shutdowns for manual cleaning, disrupting operations and increasing maintenance costs. To mitigate these issues, fuel pretreatment, particularly water-leaching, has gained attention. This process removes ash-forming elements like dirt, sand, and soluble ions. Leaching effectiveness is evaluated through fuel property analysis, pyrolysis studies, combustion characteristics, and ash fusibility tests. However, leaching efficiency varies based on biomass type, particle size, washing medium, and leaching conditions [1-7].

Utilizing heat, in terms of temperature, towards biomass structure such a practical approach could be used to study their thermal and kinetic degradation behavior. Numerous studies on the biomass degradation behavior have been carried out using the

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thermogravimetric analysis (TGA) experiments as prior knowledge of reaction kinetics and decomposition phases are able to predict and identify the trend of biomass thermal degradation according to its three polymeric constituents of cellulose, hemicellulose, and lignin [8-9]. Theoretically, the TGA is conducted in a nitrogen environment with no limitations in heat and mass transfer at low heating rates. Obtained results are interpreted as the reactivity, weight loss kinetics, and devolatilization behavior of the biomass, in particular with regard to cellulose, hemicellulose, and lignin constituents [5, 8, 10-14]. Two thermograms exhibited are likely the TG curve; which represents the weight loss of residue against temperature, and the differential TG (DTG) curve; which represents the rate of weight loss against temperature. According to the TG curve, most previous results showed that three clear drops of weight losses are able to be observed, which are mainly divided within the temperature range of (1) less than 150°C, (2) 200 to 400°C and (3) beyond 400°C, respectively [8, 12-14]. An overlapped decomposition and reaction phases of biomass polymer blocks would merge along the temperature range and cause few limitations in information in regard to determining the devolatilization regime of those lignocellulosic components. Therefore, the DTG curve could provide sufficient data to identify and differentiate the decomposition regime between cellulose, hemicellulose, and lignin components, by mainly observing and analyzing the peak present across the temperature range applied.

Washing pre-treatment effectively enhances biomass feedstock and pyrolysis product quality. This technique removes ash-forming contaminants like dirt, sand, and alkaline earth matter, significantly reducing slagging and fouling during thermal conversion processes [3, 4, 15]. Water-leaching effectively removes ash-forming elements, increasing fusion temperatures of lignocellulosic components. Multiple studies demonstrate that leached biomass exhibits delayed thermal decomposition kinetics compared to untreated samples. This shift in kinetic parameters for hemicellulose and cellulose decomposition is attributed to the reduction of ash components [7, 16-17]. Acidic washing pre-treatment significantly enhances biomass feedstock quality by effectively removing troublesome elements, particularly inorganic and metal ions, at higher rates than other washing media [18-20]. However, acid washing can negatively affect biomass structure, causing hydrocarbon bond breakage and fiber erosion. Leaching efficiency depends on the acid type, concentration, and biomass structure.

The objective of this work was to study the thermal degradation of empty fruit bunches (EFB) by carrying out common thermal analyses which are the TGA experiment. TGA experiment would generally identify and describe the decomposition behavior of lignocellulosic EFB components. A novel test setup has been engineered to ensure precise control over water washing conditions and a comprehensive collection of leached samples. The effect of the water-washing medium is examined, leading to the development of more efficient and cost-effective pre-treatment processes in biomass-to-energy conversion systems.

2 Methodology

EFB was collected from a local palm oil mill in Nibong Tebal, Penang and it was in wet condition with approximately 74.3 wt% of moisture content. Thus, biomass was oven-dried to below 10 mf wt% moisture to prevent microbial and fungal growth.

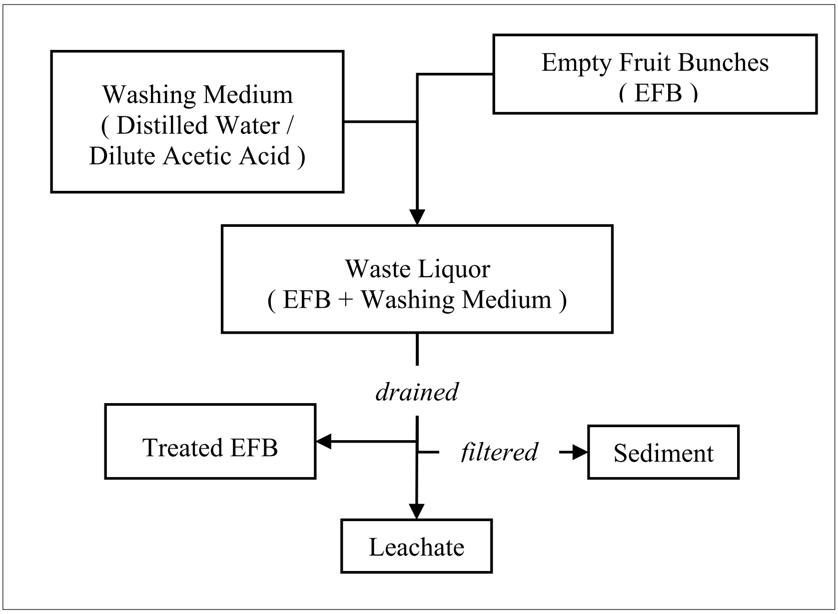

Fig. 1. Water-washing pre-treatment process of EFB.

Figure 1 shows the overall pre-treatment process flowchart of EFB. EFB undergoes pre-treatment using different washing media before fuel property analysis. The waste is soaked in either distilled water or 5% dilute acetic acid, using 1.8L of medium per 100g of EFB for 40 minutes at room temperature. The treated EFB is then drained, weighed, oven-dried, and stored for further analysis.

Investigations were conducted to assess and compare the attributes of treated and untreated EFB fuel. Moisture content, ash content, and volatile matter were analyzed for both samples according to the ASTM E871, ASTM D1102, and ASTM E872 standard test methods, respectively. Moisture content was determined after oven-drying at 105°C to constant weight, while ash content was estimated by incinerating samples in a muffle furnace at 575°C for 6 hours. The higher heating value (HHV) of both samples was determined using a Parr 6200 oxygen bomb calorimeter, following the standard test method ASTM E711-87.

Typical TG analysis of EFB was performed using Perkin Elmer TGA7, TA Instruments. The analysis was done in a nitrogen environment with a flow rate of 40-50 cm^3/min. The temperature range applied was from 25 to 900°C with a constant heating rate of 10°C/min. The trend of TG and derivative TG (DTG) curves were decisively studied in order to investigate the change of EFB weight loss and kinetic shift as a function of temperature.

3 Results and discussion

Table 1 presents the characteristics of treated and untreated EFB. The untreated EFB used in this study contains a relatively high ash content of approximately 4.07 mf wt%. The presence of a large amount of ash concentration might be due to the heavy deposition of alkaline metals and other inorganic components at the palm oil factory. With the implementation of water washing, the ash content of treated EFB soaked with distilled water and diluted acetic acid media were able to reduce by approximately 2.74 and 2.95 mf wt%, respectively. Removal rate of deposited particulate and diffusion of leachable components seem to play a major role during the leaching process. Treating with distilled water lets the ash culprits undergo a natural removal and diffusion process during the soaking period. Washing media has been observed to change in color by means most insoluble inorganic such as dirt and soil are being leached from the surface of EFB. The different conditions are observed once EFB is treated with dilute acetic acid by which tiny bubbles are released at the earlier stage of pretreatment. It is believed that the reaction between alkaline earth metals with acids causes the production of dihydrogen in the form of hydrogen gas.

Table 1. Characteristics of treated and untreated EFB.

Characteristics	Untreated EFB	Distilled Water EFB	Acetic Acid EFB
Proximate Analysis (mf wt%, dry basis)			
Ash Content	4.07	2.74	2.95
Volatile Matter	85.16	87.63	88.13
Fixed Carbon (by difference)	10.77	9.63	8.92
Chemical Composition (wt%)			
Hemicellulose	33.5	32.3	24.7
Cellulose	37.8	36.3	33.2
Lignin	21.2	20.1	18.3
Heating Value (MJ/kg)			
HHV	17.05	18.04	16.76

An earlier hypothesis is made by expecting the acid treatment to possess greater ash removal efficiencies compared to distilled water. However, based on the results, there is more reduction of ash content after being soaked in distilled water compared to the acidic media. Deng et al. [4], Tan and Wang [18], and Das et al. [19] concurred that acid treatment could lead to an apparent increase in ash percentage. This increase is attributed to the disproportionate removal of other biomass components, including extractives, hemicellulose, cellulose, and lignin. Less removal efficiencies in ash content under acid treatment might be due to the formation of molten salt mixtures in the biomass matrix. Unlike neutral media, acetic acid solution hydrolyzes the hemicellulose fraction extensively, leading to a significant reduction in hemicellulose and extractives. This results in an apparent increase in the cellulose percentage of treated EFB. The acid treatment breaks the fiber structure, causing interspaces to appear as it erodes hemicellulose first, followed by cellulose and lignin [19, 21]. Energy loss due to water washing is inevitable, as organic matter (extractives, hemicellulose, and cellulose) breaks away from the biomass matrix and enters the washing media during the process [4].

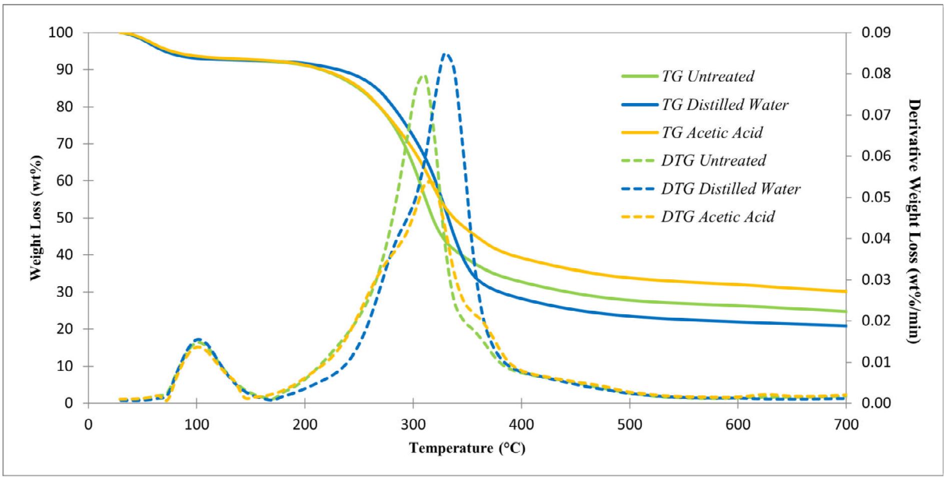

Fig. 2. TG and DTG curves from thermogravimetric analysis of treated and untreated EFB. Left-hand side y-axis: TG curves; right-hand side y-axis: DTG curves.

Thermogravimetric analysis was performed on both treated and untreated EFB to determine their thermal degradation behavior as a function of temperature between 27°C and 600°C, as shown in Figure 2. The TG curve reveals a slight weight loss for all samples in the early stage of decomposition, occurring between 90-100°C. This initial drop is primarily attributed to moisture removal from the samples [8, 13]. The pyrolytic decomposition of all samples began slowly at about 150°C with the rate increasing at about 170°C for the untreated and acetic acid EFB samples meanwhile at 200°C for distilled water EFB samples. It seems to meet the early expectation that the acetic acid EFB is decomposed at lower temperatures. It is most probably due to increasing exposed surface area towards heat compared to other samples. The interspaces created by the erosion of the primary cell wall of the lignocellulosic biomass matrix allow more surface particles to work to conduct heat. As such, the rate of heat transfer is directly proportional to the surface area through which the heat is being conducted [2, 18, 22, 23]. Devolatilization of untreated, distilled water-treated, and acetic acid-treated EFB samples was nearly complete at 700°C. The remaining residues were approximately 24.76 wt%, 20.86 wt%, and 30.09 wt%, respectively. Comparison of the remaining solid residues from both treated and untreated EFB samples indicates incomplete decomposition. This phenomenon can be attributed to their lignocellulosic composition and ash content [8].

According to the DTG curve, a pack of clear peaks representing treated and untreated EFB samples was found at temperature ranges of approximately 230 - 400°C. As reported by Burhenne et al. [8], two primary weight loss regimes are identified: the lower temperature (LT) and upper temperature (UT) regimes. The LT regime corresponds to hemicellulose decomposition and the initial stages of cellulose breakdown, while the UT regime relates to the completion of cellulose decomposition. Based on the results, both regimes seemed to be overlapped. It was found that the untreated, distilled water, and acetic acid EFB occupy a maximal decomposition rate of 0.0792 wt%/min at 311°C, 0.0849 wt%/min at 328°C, and 0.0530 wt%/min at 319°C, respectively. In addition to that the curve for both treated samples has slightly shifted to higher temperatures compared to the untreated samples. This result suggests that treated samples require higher activation energy for decomposition, a phenomenon attributable to the altered catalytic effect of the reduced ash content. The presence of ash in biomass may act as a catalyst once influenced by heat. The ash exhibited higher activities in depolymerization, decarboxylation, and cracking of lignocellulosic composition over a temperature range of 200 - 700°C that caused significant differences between treated and untreated samples on their weight loss characteristics and temperature regimes of molecular structure decomposition [6, 14].

4 Conclusion

The impact of water washing on fuel properties and thermal degradation behavior has been comprehensively analyzed, yielding significant insights. Implementing distilled water and acetic acid treatment on EFB is sufficient to effectively remove the ash content by approximately 2.74 and 2.95 mf wt%, respectively. TGA results show significant effects of the depolymerization, decarboxylation, and cracking profiles of lignocellulosic composition between treated and untread samples. Understanding two key factors can provide valuable insights for industry process improvements: (1) the changes in heat transfer through interspaces of disrupted fiber structures, and (2) the catalytic effect of ash on lignocellulosic decomposition. These insights can significantly enhance waste management, reduce emissions, and improve resource efficiency.

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