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TGA Study on Catalytic Thermal Degradation of Brown Solid (Fermented Product from Rice Straw) and Ash from Brown Solid as Catalyst

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ABSTRACT

Biomass is all parts that come from living creatures, such as plants. Biomass waste, especially from plants, has an energy source that can be converted into energy or chemicals. Biomass can be used as a renewable energy source, processed through thermal processes that convert biomass into renewable energy, such as the pyrolysis process, which produces gas, bio-oil, and biochar. Biochar is a black solid resulting from pyrolysis and contains many natural minerals depending on the biomass. Abundantly available biomass waste is rice straw. Brown solid is a fermented product from rice straw, one of the most abundant biomass. The high ash content in biomass has not been utilized optimally. The ash contained in biomass is a natural mineral that can be used further, such as as a catalyst. In this research, biomass ash from brown solids was used as a catalyst for thermal degradation by being characterized using TGA analysis to see the nature of thermal degradation and SEM analysis of charcoal or char and ash from brown solids. Brown solid pyrolysis products produce char heated to obtain ash that can be used as a catalyst. Thermal characterization of ash degradation as a catalyst and brown solid was carried out at biomass to ash as catalyst ratios of 1:1, 1:2, 1:3, and 1:4. The 1:1 ratio of brown solid to ash as catalyst has the most mass loss compared to other ratios. SEM analysis of brown solid ash shows significant differences in shape. The morphology of brown solid ash is like flakes.

1. Introduction

In the future, biomass has good potential as a raw material for synthesizing chemical and liquid fuels [1]. The Biomass residues commonly utilized for energy generation are rice straws and rice husks. The main constituent components of biomass are cellulose, hemicellulose, and lignin. Cellulose and hemicellulose consist of glucose units arranged into complex polysaccharides. Natural materials such as plant or tree stem waste, waste from the agricultural industry, and agricultural waste, which is usually only burned, the materials mentioned are biomass. Biomass is currently the largest renewable energy source containing the world's largest carbon content and resources, and it is the only renewable source of carbon for use in chemicals and materials. Rice straw crop residues refer to rice plant residues that persist along the field after the collection of crops. Brown solid is a rice straw waste product fermented using cellulose ethanol. Fermented rice straw, called brown solid, is the raw material used to produce pure cellulose. Brown solid was obtained from the Far Eastern New Century Research and Development Center, Taiwan [2]. Most of the rice straw is produced in Asia. It is about 91% of worldwide production. Eastern Asia, which includes China and Taiwan, is the highest producer of rice straw, with 32% [3]. Meanwhile, based on data from the Central Statistics Agency (BPS) in 2022, Indonesia has a rice harvest area of 10.61 ha with a total rice production of 55.67 million tons. Indonesia is an agricultural country rich in agricultural products, plantations, forestry, livestock, and fisheries. These natural conditions provide great opportunities for Indonesian people to do business in the agricultural sector. One of the largest agricultural products in Indonesia is rice. The large value of the rice harvest will produce waste such as rice husks and straws. The availability of rice straw waste reaches around 55 million tons a year, but only around 31-32% of it is used as animal feed [4]. Biomass degradation is a thermochemical process that breaks complex carbon bonds. Biomass consists of cellulose, hemicellulose, and lignin. These components have differences in thermal degradation characteristics, where hemicellulose is degraded more quickly, and cellulose and lignin have higher degradation temperatures. Cellulose and hemicellulose are mostly volatile, while the lignin pyrolysis products are mostly light gas and charcoal [5]. Biomass depolymerization is a process that breaks down the complex C-C bonds into simple compounds that can be used to make commercially important chemicals and biofuels. The thermal degradation properties of biomass can be observed using a Thermo Gravimetric analysis (TGA) test before it is applied to the pyrolysis process or further processes.

Thermo Gravimetric analysis (TGA) has been widely used for thermal degradation or decomposition of biomass in terms of overall mass loss rate. Thermo Gravimetric analysis (TGA) is an important instrumentation tool used to determine the thermal degradation properties of a material. TGA is used to characterize the thermal properties of materials used in various pharmaceutical, food, environmental, metals, petrochemical, and polymer applications. A TGA is only as good as its ability to accurately and reproducibly measure mass in function of time or temperature changes. These properties can be determined from either weight gain or weight loss. The analysis of brown solids by TGA in the previous study showed that about 0.9% of the mass was lost in the first step, indicating water content. The weight loss of about 41% in the first peak on DTG (Differential Thermo Gravimetric) shows the degradation of cellulose, hemicellulose, and lignin [6]. The last step was to lose weight by about 11% [2]. The weight loss of rice straw starts at around 190–200°C and slows down at 400°C before reaching the final temperature. Solid residue or char yield was about 27% of the feed [7]. The dehydration zone on TGA of rice straw in the 60–190°C temperature range indicates water evaporation. The second region is the corresponding polymerization of hemicellulose and cellulose in the 190–390°C, and the DTG curve indicates that the temperature peak of the higher temperature zone, and the last region is the depolymerization of lignin in the more than 400^{o}C [8]. The pyrolysis process occurs in a temperature range of around 450 K to 600 K. The pyrolysis process starts at a temperature of 450 K to a temperature of 600 K. Then, the sample experiences a slow weight loss until the temperature reaches the final temperature of the pyrolysis. The final yield of biochar residue is around 30% for rice straw [9]. TGA data from rice straw with catalyst ZSM-5 and without catalyst in the first step is the same; in the second step on the addition of the catalyst, the temperature of maximum mass loss rate was reduced, and in the last stage, the final temperature decomposition [10]. Rice straw contains high levels of silica (SiO_2) and alkali metals, causing negative impacts such as fouling, erosion, agglomeration, slag, and scale in heating systems. Scaling and slagging occur during fuel combustion at higher temperatures [7]. The major component of ash from brown solids is SiO_2 [2]. Catalytic brown solid to spent catalyst with ratios 1:1, 1:2, 1:3, and 1:4. The overall weight loss for the brown solid to catalyst (1:0) and (1:4) is 42.4% and 44.0%, with the temperature range in the degradation of 200 – 400°C [11]. The results of the previous research indicate that the brown solid could be degraded using a catalyst during the thermal decomposition process. In this research study, the thermal degradation of brown solids to catalysts with ash as a catalyst in different ratios 1:1, 1:2, 1:3, and 1:4 used a TGA instrument.

2. Research Methodology

2.1. Materials

Materials used in the research were brown solid from Far Eastern New Century Research and Development, Taiwan. The ash used in this research came from a calcined brown solid.

2.2. Procedures

This research has 2 stages, and the first is the formation of ash from a brown solid using a calcination process in a furnace. The research procedure is ash from char or solid product pyrolysis of brown solid, and then the char was calcinated at 400ºC for 2 hours and continued calcination at 900ºC for 6 min [2]. Furthermore, after obtaining pure ash from brown solids, the ash is used as a catalyst for thermal degradation using a TGA tool with varying ratios of catalyst and brown solids. The thermal degradation of brown solid to ash with ratios 1:1, 1:2, 1:3, and 1:4 by using the TGA instrument (TA Q50, USA), approximately 10 mg of samples were placed in a platinum plate, heated in a nitrogen environment at 30°C for 3 min to stabilize. Then, the sample was heated from 30°C to 600°C at 5°C/min under a nitrogen atmosphere at 40 mL/min. In this study, SEM (JEOL JSM – 5600, Japan) was used to analyze the microscopic structure of ash.

3. Results and Discussion

3.1. Yield of Ash

Solid product from pyrolysis brown solid <60 from the total product pyrolysis [2]. In the biochar product, the organic component is still there, and the char of brown solid is rich in carbon, as shown in Fig. 1(a). Brown solid has a fixed carbon content of 24%, volatile matter of 56%, and ash of 20% [11]. The char product of brown solid calcined under air at 400ºC yields 40.47% from the feed. Calcined char of brown solid at 400ºC, the color was grey, as shown in Fig. 1(b). This finding indicates that there is still carbon content, and the mass loss of rice straw between 345°C and 500°C was 15% residue. The residues from DSC and TGA analyzed showed gray, indicating the carbon content was incomplete oxidative decomposition [12] and the ash was not melting when calcination at 900ºC for 6 min, as shown in Fig. 1(c). the yield was 84%, and the color was white.

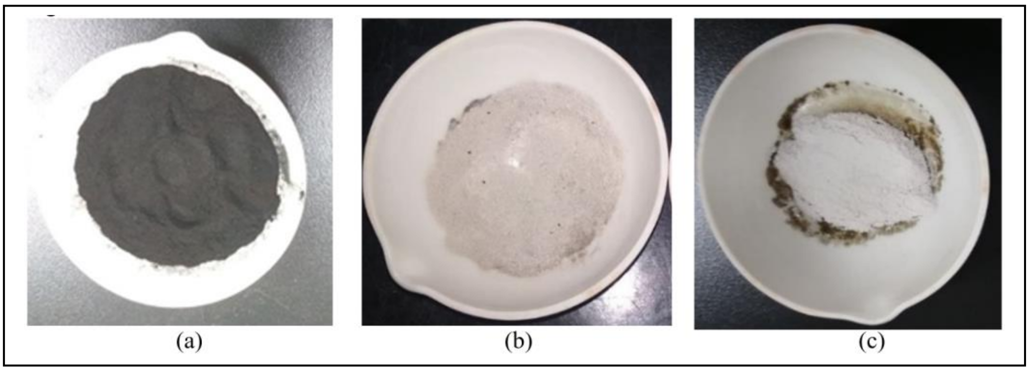

Fig. 1. Char of brown solid changes to ash. (a) Char product from pyrolysis of brown solid. (b) Calcined char of brown solid at 400°C. (c) Calcined ash from brown solid at 900°C.

The sample is white, indicating the remaining minerals resulting from calcination. The elements carbon and hydrogen are elements that have evaporated from the sample. Carbon and hydrogen are the main elements of biomass. Brown solids from rice straw, where SiO_2 is the most component in ash, SiO_2 has a melting point of more than 1500°C. Furthermore, ash of brown solids does not melt at 900ºC.

3.2. Thermal Degradation of Brown Solid and Ash From Brown Solid With Variations in Mass Ratio

Thermal degradation of brown solid to ash (1:1, 1:2, 1:3, and 1:4) is given in Fig. 2. DTG (Differential Thermo Gravimetric) is given in Fig. 3. TGA measures the weight loss of the sample in the function of temperature changes. The effect ratios of ash in the degradation of brown solid (BS) are in Fig. 2. Principally thermal degradation used TGA has three stages process; the first stage for removed water content in all ratios of ash is the same at temperatures 100-200ºC and the weight loss is about 1.5%. The second stage is the corresponding degradation of hemicellulose and cellulose at a range temperature of 200-380ºC. The evolutions of volatile organic compounds at 230 and 315°C for TGA analysis of rice straw [13]. The effect of the ash ratio on weight loss can be seen in Fig. 2 and Fig. 3.

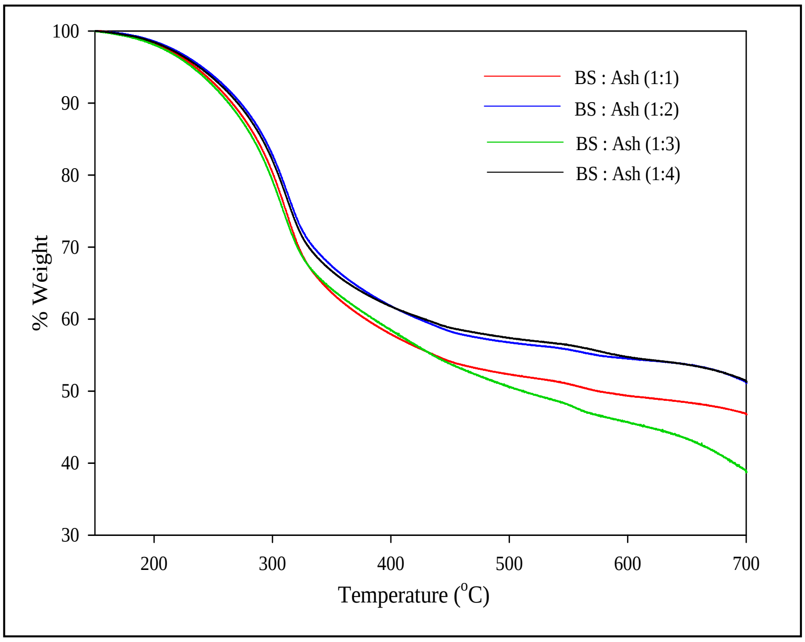

Fig. 2. TGA curves of the catalytic degradation of brown solid with ash from brown solid as catalyst.

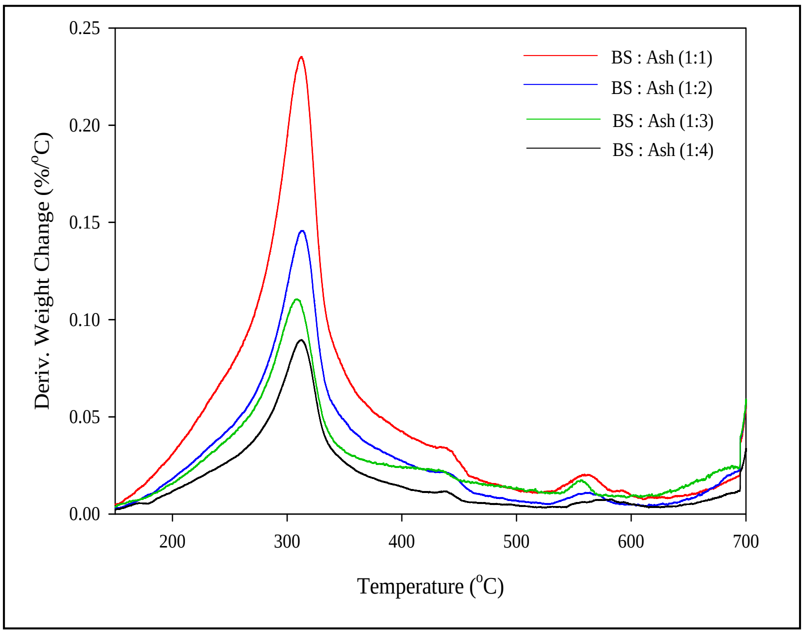

Fig. 3. DTG curves of the catalytic degradation of brown solid with ash from brown solid as a catalyst.

The weight loss of brown solid to ash (1:1) is more weight loss than other ratios. The ratio of brown solid to ash (1:1) is a weight loss of about 43%; the ratio (of 1:2), the weight loss is 38%; the ratio (of 1:3), the weight loss is 40%, and the ratio (of 1:4) is 37%. Compared to previous research, TGA analysis on brown solid without using a catalyst showed a weight loss of 42.4% [2] and TGA analysis of brown solid with spent catalyst at a ratio of 1:4 was the highest weight reduction compared to other ratios of 44% [11], this is also proven when the addition of a catalyst will increase the resulting depolymerization product [14]. As observed in Fig. 3, DTG curves showed the highest peak at a ratio of 1:1 compared to the others, so this ratio has the greatest mass loss. The most weight loss happened in this stage, and DTG peaks show the temperature at 310°C in Fig. 3, which is the volatile compound. Pyrolysis of rice straw using a batch reactor at a temperature of 300°C produces the most bio-oil products compared to temperatures of 250, 350, and 400°C [15]. This is in line with the DTG curve, which shows the highest peak, which means the most mass loss is at a temperature of 310°C. Cellulose and hemicellulose are sources of the formation of volatile components, which are then condensed to produce bio-oil [16].

The last stage is char formation, which slowly decreases the temperature. The last weight corresponds to the fixed carbon. The third stage is the formation of char, which is the slow release of the brown solid at 538ºC [2]. Degradation was also observed between 370°C and 470°C as a process of breaking carbon bonds in lignin and also oxidation of decomposition products from the previous stage [17]. The carbon converted into biochar or fixed carbon, which comes from lignin, is the final product of this process. Biochar is difficult to evaporate at a pyrolysis temperature of around 500ºC [16]. Lignin has strong cross-links and consists of polysaccharides that have benzene-propane-type monomers. Lignin is difficult to decompose, so it has high thermal stability [18]. However, the lignin content in rice straw is only 12-24% [19], with more hemicellulose and cellulose content. Furthermore, the fixed carbon in a brown solid is 24% [11]. In Fig. 2, the final carbon is 50% at ratios 1:2 and 1:4, while the lowest carbon at ratio 1:3 is 38%, and at ratio 1:1 is 47%. Pyrolysis of rice straw at a temperature of 400ºC obtained a char product of 38% [15]. The rice husk (4.887 mg) and rice husk ash (7.188 mg) samples were analyzed on the TG; the samples had a small weight loss of 9 wt% in temperature 150°C, and the TG analysis of rice husk ash reported a mass loss at about 500°C (approximately 39.6 wt%), corresponding to the loss of carbon still in the ashes [20]. Thermal degradation of biomass using a catalyst can increase the product. Upgrading bio-oil from lignin pyrolysis can use catalysts such as SiO_2/Al to produce many phenolic products [21]. It was found that the activation energy of ketenization decreased by using a SiO_2 catalyst in the Kinetics of Valeric Acid Ketonization and Ketenization [22]. The use of catalysts in biomass degradation can increase product and reduce activation energy [11].

3.3. Analysis SEM of Ash from Brown Solid

The morphology of the brown solid is shown in Fig. 4. Viewed from 5000x magnification in Fig. 4, the particles are more unified, and the particle shape is sharp. Morphology from SEM analysis of biomass ash illustrating amorphous structure in the form of agglomerated particles with irregular shapes.

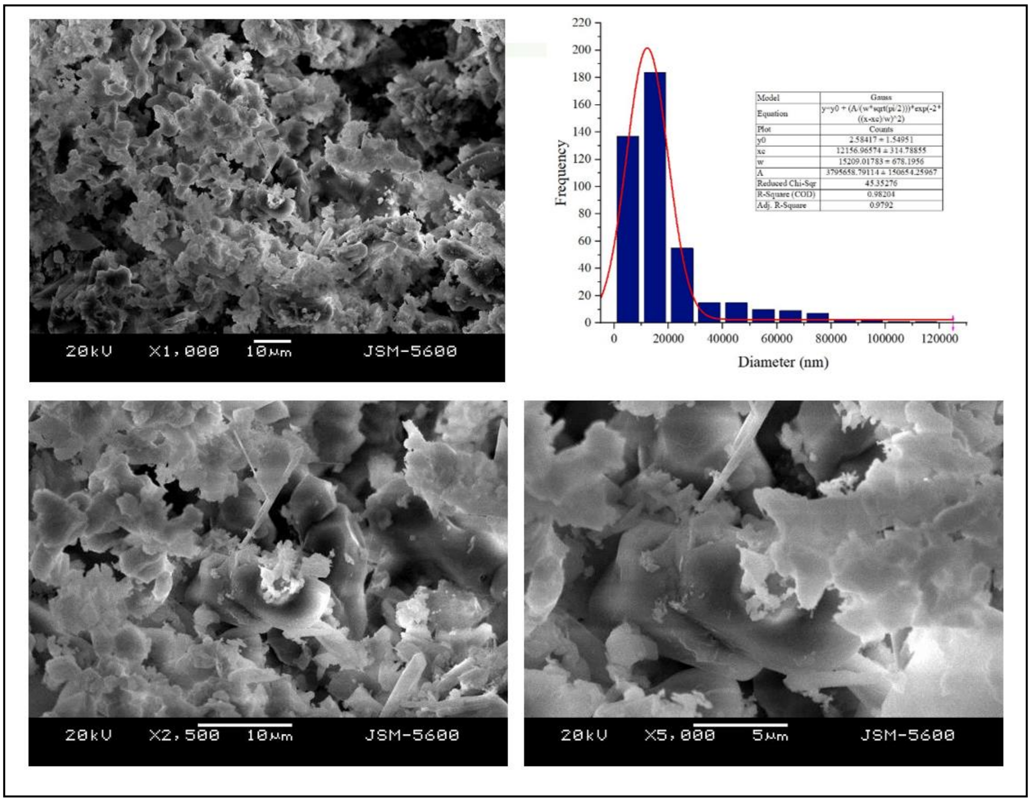

Fig. 4. Analysis SEM of ash brown solid.

Meanwhile, the morphology of biomass ash shows a flake-like microstructure. Microflake structures are generally more suitable for catalytic applications than other metals [23]. Volatile substances in the pyrolysis process leave the system, causing the charcoal surface to become rough and the number of pores to increase. The surface of the pores shows the characteristics of an irregular shape [5]. The particle size distribution between biochar and brown solid ash is significantly different; the particle size of brown solid ash is smaller than that of brown solid biochar. This is clear because the ash from brown solid no longer contains hydrocarbon and is a pure mineral, mostly SiO_2 compounds [2]. Char biomass samples at temperatures of 500ºC and 600ºC show a smooth surface, and the particle shape is similar to that of biomass particles. after heating at 1200°C and 1400°C, the particles' surface shape at these temperatures is modified due to sintering, indicating an increase in the percentage of minerals [24]. The catalyst used to assist the pyrolysis process, which has a small size, will be better because the smaller the size, the wider the contact, so the reaction process will be better [11].

4. Conclusion

Ash from brown solids can be used as a catalyst for thermal degradation. In this study, a brown solid-to-catalyst ratio of 1:1 had the greatest mass loss compared to ratios of 1:2, 1:3, and 1:4. TGA analysis is used to see the thermal properties of biomass. The TGA graph shows three stages. The first is the loss of water content in the brown solid. The second stage is the largest mass loss. in the second stage, a graph shows the volatile components. Meanwhile, char formation is used for the third graph. The morphology of the ash from the brown solid is sharp.

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