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Thermogravimetric assessment for combustion characteristic of torrefied pellet biomass from agricultural solid waste

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Abstract This present paper is focused on the investigation of combustion characteristics of torrefied pellet biomass from agricultural waste. Four biomass pellet samples such as sugarcane bagasse, Napier grass, Palm Empty Fruit Bunches, and Cassava stem were torrefied in a designed cylinder tubular pyrolysis reactor. The reactor was set up under 30 min of residence time, and the temperature reaction was varied at 200, 250, and 300 °C in an inert atmosphere. The torrefied products were then characterized in terms of their psychochemical properties such as proximate, ultimate, calorific value, and combustion properties. The combustion properties of raw and torrefied biomass pellets during the combustion process were investigated by the thermogravimetric analyzer Exstar SII TG/DTA7300. The samples were heated at an ambient temperature up to 800 °C at a constant heating rate of airflow at 10 °C/min in airflow. The results showed that the moisture content and volatile matter of torrefied pellets decreased by 2 to 5% and 8 to 14%, subsequently. Otherwise, the fixed carbon content is up to three times higher than the raw material. The study conclusively that torrefaction can also able to enhance combustion performance in terms of ignition and burnout temperature, ignition and burnout index, and combustion rate. The results shows that, the ignition and burnout temperatures of torrefied pellets are higher than raw material. The ignition and combustion index of torrefied pellets are lower than raw material, and the torrefied pellets have a longer burning time and a higher combustion temperature.

Keywords: Torrefaction, Pellet Biomass, Thermogravimetry Assessment, Combustion Properties, Solid Biofuel

1. Introduction
Lampung province is one of the provinces in Indonesia that prioritizes economic development from the agricultural and plantation sectors. So that, Lampung province plays an important role in the fulfillment of food, raw materials for the agricultural industry and plays an important role for the national economy. Lampung has long been history as one of the national barns in Indonesia, which is supported by production of plantation crops such as palm, rubber, sugar cane, and Acacia mangium; while for food crops through production of commodities such as rice, maize, cassava and so on. Due the huge agricultural commodities, Lampung has a lot of biomass resources. Most of the biomass found is Oil palm waste (OPW) (empty fruit bunch, mesocarp fiber, frond, trunk, and palm kernel shell), napier grass, sugar cane bagasse, cassava stem, and so on.

Biomass has been used for a long time as fuel, but direct use of biomass as combustion fuel has been ineffective, due to its water content, high volatile matter, low calorific value, and low combustion efficiency [1]. Hence, it is necessary to improve thermal characteristics such as torrefaction.

Torrefaction is one of several processes to improve the characteristics of biomass. It involves modification of physical and chemical composition. This process consists of heating the biomass at temperatures ranging from 200℃ - 300℃ in inert atmospheric conditions. Torrefaction caused most of the hemicellulose and cellulose loss to volatilize as well as products with a higher energy density and calorific value [2,3]. Several previous studies have shown that torrefaction of biopellets can increase the calorific value and energy density values compared to raw material. The torrefied biopellets are good feed for gasification and combustion [2,3,4,7,8,9].

The torrefaction process can decrease the oxygen (O) and hydrogen (H) content, with the final product having a lower oxygen-carbon (O/C) ratio and hydrogen-carbon values (H/C) ratio [5,6]. In previous studies [6] had carried out the torrefaction process using biopellets of oil palm empty fruit bunches. Results of the study have explained that torrefied biopellet had lower H/C and O/C values due to deoxygenation, dehydration, and carbonization reactions. Solid fuels with low H/C and O/C values will produce higher combustion efficiency so that torrefied biopellets are felicitous for fuel.

As far as we know, there was no litery study focused on evaluating the characteristics of combustibility (such as temperature and time of ignition, temperature and time of burnout, and heating rate) on pellets of EFB, sugarcane bagasse, cassava stems, and nappier grass after torrefaction process, especially at torrefaction temperature of 200℃, 250℃, and 300℃. Whereas, the combustion characteristic is fundamental knowledge for choosing parameters design of thermochemical systems

Based on the above-mentioned, this study aims to evaluate the effect of the biomass pellet before and after the torrefaction process to their combustibility characteristic. The evaluation consists of combustion characteristics such as time and temperature of ignition, time and temperature of burnout, and combustion rate, including calorific value and proximate analysis. The evaluation of combustibility method was conducted by using a thermogravimetric analyzer. Thermogravimetric analysis (TGA) is the most greatly used thermal analytical technique to provide precise information about the weight loss profile during biomass combustion (reduction or increase weight) with time or temperature [2,3,7].

2. Materials and methods

2.1Sample preparation and torrefaction process

Four samples that were obtained from pellet industries, such as empty fruit bunches (EFB), sugar cane bagasse, cassava stem, and napier grass were used in this experiment. Cassava stem biopellet, sugarcane bagasse biopellet and napier grass biopellet came from PT. Toyota Bio Indonesia and empty fruit bunches (EFB) derived from PT. Toba Hijau Sinergi. The sample of biopellets was being torrefied used a tubular type torrefaction reactor under inert conditions. The torrefaction process was carried out at temperatures of 200ºC, 250ºC, and 300ºC for 30 minutes.

2.2Characterization of pellet

The biopellet samples before and after torrefaction treatment are characterized by using several analysis methods, included proximate analysis (ash content, moisture content, fixed carbon value, and volatile matter), and calorific value. The procedure used for the characterization analysis was carried out as follows:

Proximate analysis was determine following the standard ASTM E-870-82 [15]. Moisture content is calculated from the total weight loss of the sample during heating at a temperature of 105°C until the sample weight is constant. The ash content is heated at a temperature of 575°C for 3-5 hours. The volatile matter is calculated from the total weight loss of the sample during heating, and the mass of the residual sample is calculated as the fixed carbon value. The analysis of volatile matter was carried out at a temperature of 950°C for 7 minutes. Calorific value analysis was determined by using Dulong's formula [10].

$$HHV\ (MJ\ kg^{-1}) = 0.3383C + 1.442\ (H - O/8) \quad (1)$$

Where C, H, and O is carbon, hydrogen, and oxygen content following standard ASTM D5373-02 [16].

2.3 Thermogravimetric analysis
Thermogravimetric Analysis (TGA) was following procedure of dry ashing method (dry ashing) with some modification [12]. The thermogravimetric analysis was calculated based on weight loss of sample during total time. Thermogravimetric used in this investigation was thermogravimetric analyzer Exstar SII TG/DTA7300. Thermogravimetric (TG) and differential thermogravimetric (DTG) were performed with 5-10 mg samples which heated at an oxygen atmosphere with flow rate at 100 ml/minute and heating rate at 10 ℃/minute. The temperature ranged from 25°C to 800°C.

2.4 Performance index
The performance index was also investigated in this paper, the performance indices considered are ignition index (Di) and burnout index (Db). The mathematical equation for these respective combustion performance index are expressed as follows Eqs. 2 and 3 [2,12,13,14].

$$Di = \frac{DTG\ max}{tmax \times ti} \tag{2}$$

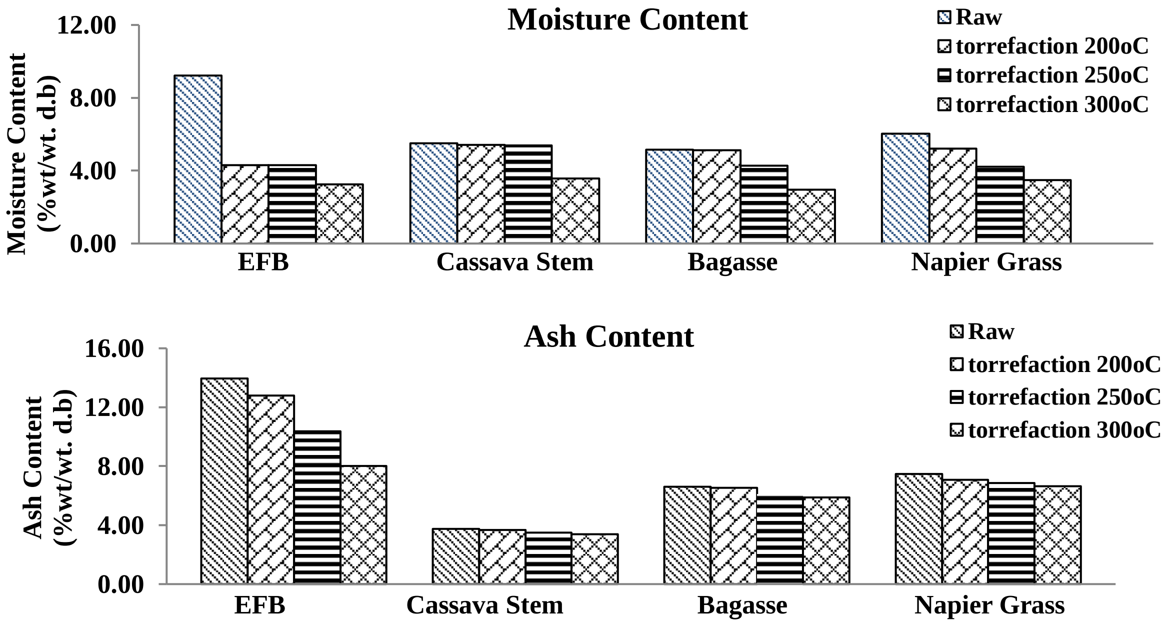
$$Db = \frac{(DTG\ max)}{\Delta t_{1/2} \times\ tmax \times tb} \tag{3}$$

Where :
DTG_{max} is the maximum weight loss rate (µg/s),
DTG_{mean} is the average weight loss (µg/s),
tb is the burnout time (minutes),
Tb is the burnout temperature (°C),
ti is the ignition time (minutes),
Ti is the ignition temperature (°C),
t_{max} is the maximum weight loss time (minutes), and
$\Delta t½$ is the time range at the half value of DTG_{max} (minutes). [2,12,13,14].

3. Result and discussion

3.1Physicochemical characteristic result
Figure 1. shows that the moisture content of biopellet decreases after torrefaction. It was very clearly observed that EFB pellet has higher water content than other samples. However, the moisture content slowly decreases along with the increase of torrefaction temperature. The standard of biopellet stated that the maximum of moisture content of biopellet is about 12% [17]. This result concluded that torrefaction able to evaporate all of the free water of biopellet and make the biopellet becomes drier. According to storage purposes, the torrefaction process makes biopellet more durable for storage and is not too easily decomposed or flammable.

Another criteria of solid fuel is low ash content, because a high ash content can reduce the calorific value and triggered the slagging and fouling problems in furnace. Figure 1 shows that the torrefaction process is proven able to reduce the ash content and making torrefied biopellet qualified to use as a fuel. The ash content of torrefied biopellet has met the European biopellet standard [18] of 0.5-10%.



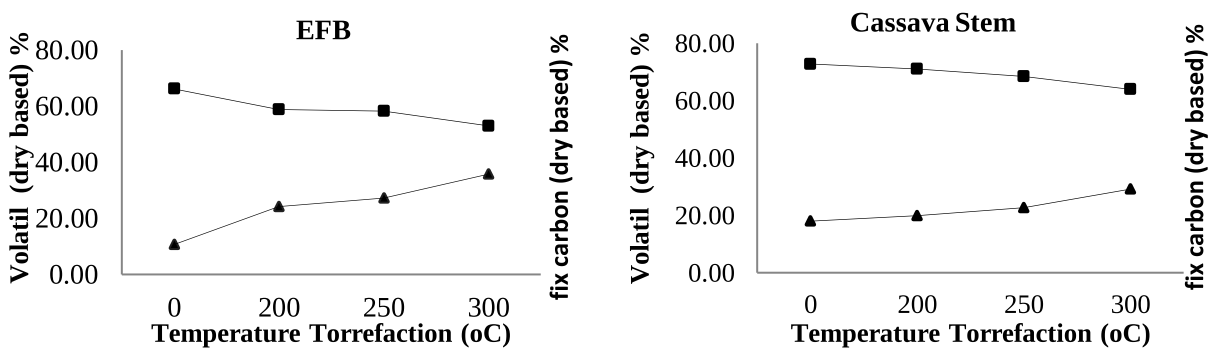
(a)

(b)

Figure 1. (a) Moisture content (b) Ash content of raw biopelet and torrefied biopelet

As well as with moisture content and ash content, Figure 2 Shows that the volatile matter content of biopellet decreases after torrefaction. The volatile matter of biopellet has met the standard for wood pellets [17] which is max. 80%. The volatile matter of biopellet is depended on the carbonization process during the torrefaction. An increase of torrefaction temperature is able to remove volatile matter.

Inversely proportional to volatile matter, fixed carbon has increased after torrefaction process. The high percentage of fixed carbon value makes it difficult to burn and need longer time to burn out. The fixed carbon value of torrefied biopellet has qualified the standard for wood pellets [17] of at least 14%.



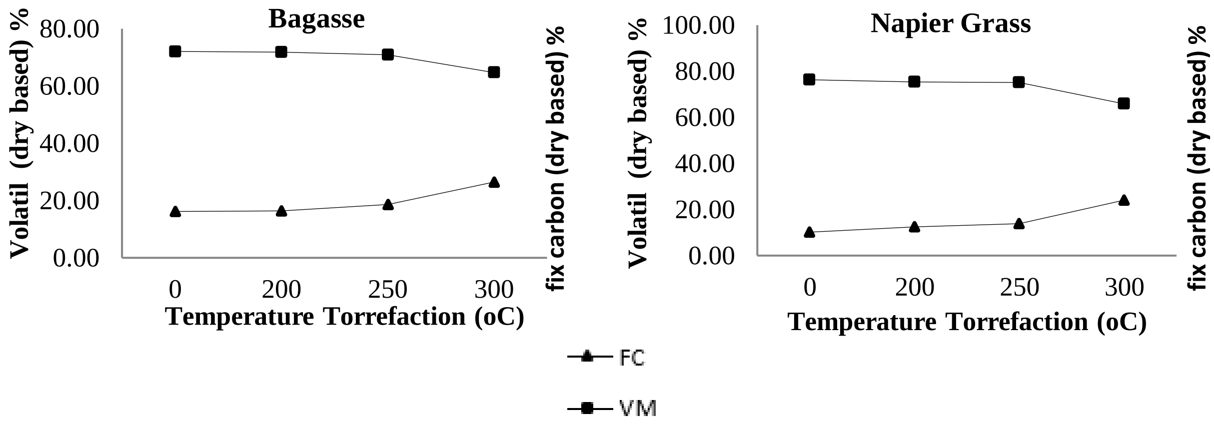


Figure 2. Volatile matter and fix carbon of raw biopelet and torrefied biopelet.

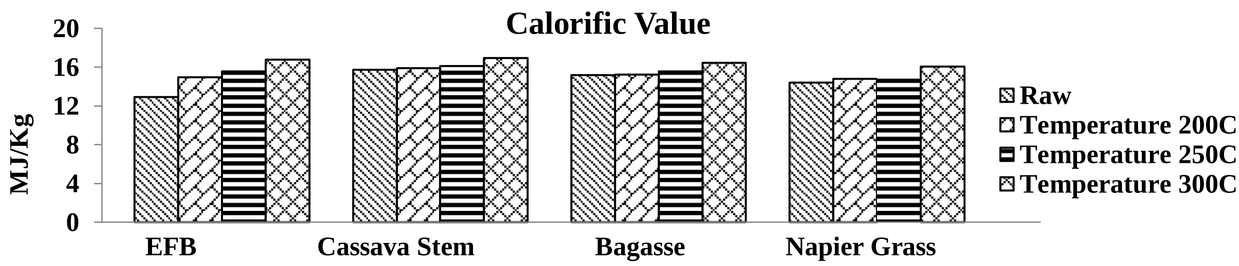


Figure 3. Calorific value of raw biopelet and torrefied biopellet

The calorific value aims to determine value heat combustion of fuel. In addition, the calorific value is one of the main parameters in determining the quality of fuel.

Figure 3. shows that torrefaction can increase the heating value of biopellet. The calorific value of torrefied EFB and cassava stem biopellet 300°C has qualified the standard for wood pellets [17] of at least 16.7 Mj/Kg. The results of this study are in line with previous research conducted [6] torrefied biopellets has increased from 15.82 Mj/kg to 17.90 Mj/kg. This case is due to the increased carbon content in the biopellet.

The calorific value needs to be known to determine the value of the heat of combustion that can be produced by biopellets as fuel. The higher the torrefaction temperature, the higher the calorific value due to the effect of the high carbon content bound to the biopellet. This is because the combustion process requires carbon which will react with oxygen to produce heat.

3.2Thermogravimetric Analysis

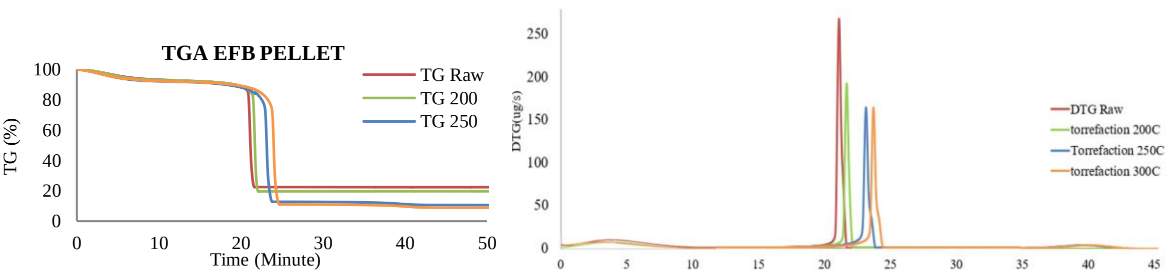


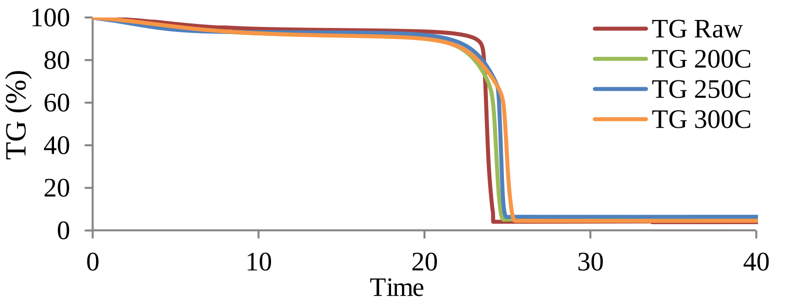
Figure 4. TG-DTG profile of un- and torrefied biopellet in varied torrefaction temperature condition

Figure 4 shows that combustibility properties changed after the torrefaction. Compared with untorrefied pellet, the torrefied pellet have longer time to ignite and higher ignition temperature. The untorrefied with high volatile content easier to ignite then the biopellet with low volatile content. In EFB pellets before torrefaction has ignition time about 15.55 minutes and temperature about 167.98℃. While, torrefied EFB biopellet at temperature of 300℃ has ignition time about 19.98 minutes and temperature about 214.38℃. the result shows that the torrefaction able to increase the ignition time and temperature due to its proximate value.

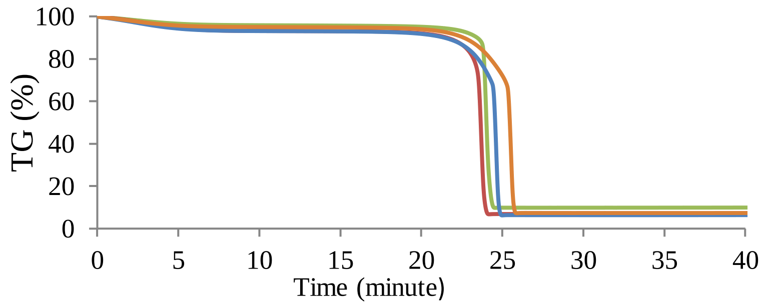
As well as ignition time, time of burnout also has increase. Un-torrefied biopellet have time burnout at 22.11 minutes and temperature at 265.95℃ more lower than torrefied biopellet at temperature of 300℃ which have burning time runs out at 26.84 minutes at a temperature of 285.67℃ .

Torrefaction process reduces moisture content, reduces volatile matter and ash content which makes the first stage of combustion take longer. What remains in biopellet after torrefaction process is fixed carbon and small amount of moisture and ash content. So that biopellet has difficult to burn.

Of all torrefied biopellet samples, EFB pellets at a temperature of 300℃ is the longest burning time. It is have ignition at 19.98 minutes with 214.38°C as well as burn out at 26.84 minutes with 285.67℃. This is because fixed carbon value of 300℃ EFB biopellet is the highest among other biopellet.



(a)



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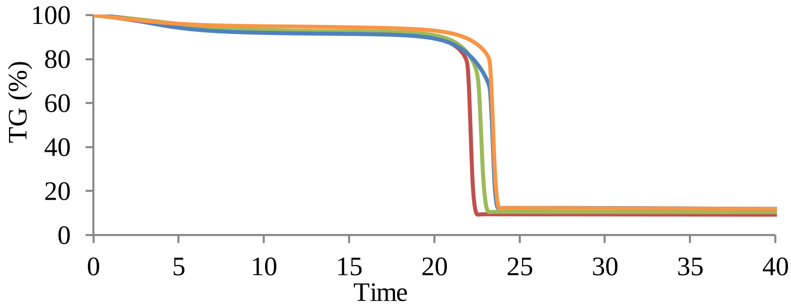

(c)

Figure 5. TG profile of un- and torrefied biopellet in varied torrefaction temperature condition (a) cassava stem biopellet (b) baggase biopellet (c) napier grass biopellet

In addition to decrease weight with time and temperature, from the thermogravimetric analysis also can obtained the rate of reduction sample mass during the combustion process (dm/s). DTG is a type of thermal analysis where the rate of change in weight of material when heating is plotted between time/temperature (dm/s) is used to simplify readings of peak combustion. dm/s can also be called combustion rate [2,3,7,12].

Figure 6. explained several stages in the thermogram during the combustion process. The first stage is drying which is characterized by a slow decrease of weight loss. This stage occurs at a temperature of 100℃. The second stage is devolatilization which is characterized by a very rapid decrease of mass. This stage occurs in range temperature 150℃ – 405℃. The third stage is carbonization which is characterized by a decrease in mass which slows down again until the sample becomes carbon and ash.

Figure 6. obviously explained that torrefaction able to improve the biopellets as a solid fuel. The elevated combustion temperature with high weight loss rate implies improved combustion. The evaluation combustion rate is carried out to determine the effectiveness of a fuel. This methode to determine the ability of fuel for can be used in its application.

The greater burning rate then the faster biopellet will burn. While what is expected from the fuel is biopellet that burns for a long time.

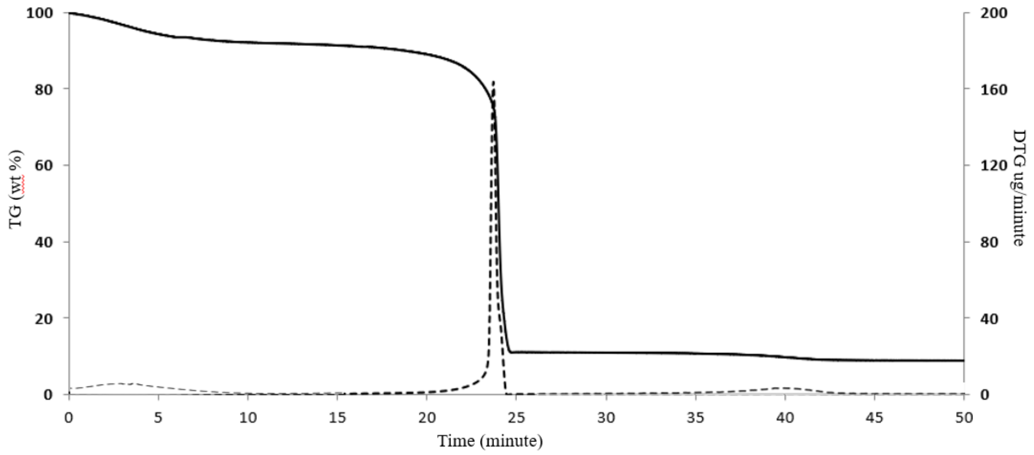

Figure 6. TG – DTG profile of EFB biopellet after torrefaction 300◦C

Figure 6. shows EFB biopellet temperature 300◦C have three stages of weight loss. The first stage is evaporation of water content. The second stage is oxidation and removal of sample volatiles. The third stage is the oxidation of the remaining charcoal at a relatively high temperature burning of combustible materials. While in raw biopellet, there are two stages of decomposition. The first peak is defined as the de-volatilization stage and the second peak is defined as the burning of lignin and charcoal. At this stage, the chemical bonds are broken thermally and what's left is carbon.

It can be seen that torrefied EFB biopellet experienced a significant change compared to the raw biopellet, the reactivity of torrefied biopellet is decreased, resulting in higher ignition and combustion temperatures over a wider temperature range.

The combustion rate of raw EFB biopellet is 267.5696 ug/s and the burning rate of torrefied biopellet at 300◦C has decreased by 161.3243 ug/s, which means that torrefaction makes torrefied biopellet burn for 161 micrograms per second from 267 micrograms per second.

Same common also happened to bagasse pellet, cassava stem and napier grass pellet. There was a decrease combustion rate. In table 1. there are changes in burn time and temperature. The torreffed biopellet had an increase temperature and time. This value indicates that biopellet before torrefaction process is more difficult to burn. Biopellets with high ignitability or non-combustibility have advantages in storage process, meaning that they can be stored for a long time without the risk of burning if stored in direct sunlight. According to purpose, torrefied biopellet will more durable to store and the biopellet will not decompose or flammeable easily.

Table 1. Time and temperature combustion

Sample of biopellet	ti (min)	tb (min)	DTG max (μg/s)	Ti (°C)	Tb (°C)
EFB Raw	15.55	22.11	267.5686	167.98	265.95
EFB 200 ℃	17.01	22.38	191.8876	194.02	266.11
EFB 250 ℃	17.87	24.27	163.7973	203.41	270.11
EFB 300 ℃	19.98	26.84	161.3243	214.38	285.67
EFB 250 ℃	17.87	24.27	163.7973	203.41	270.11
EFB 300 ℃	19.98	26.84	161.3243	214.38	285.67
Cassava stem Raw	19.65	23.50	218.3594	223.10	316.81
Cassava stem 200 ℃	19.75	24.95	200.0879	225.60	320.09
Cassava stem 250 ℃	20.49	25.00	187.6865	232.66	350.38
Cassava stem 300 ℃	21.12	25.52	148.6852	239.70	365.74
Bagasse Raw	18.55	24.58	264.0346	210.49	299.77
Bagasse 200 ℃	18.81	24.39	246.1285	214.03	301.28
Bagasse 250 ℃	18.91	25.24	200.0879	214.36	301.57
Bagasse 300 ℃	19.93	26.21	165.979	225.71	307.25
Napier Grass Raw	19.10	22.65	208.8324	217.02	314.43
Napier Grass 200 ℃	19.23	23.52	174.9481	218.19	345.74
Napier Grass 250 ℃	19.71	23.86	134.7127	224.61	349.94
Napier Grass 300 ℃	19.85	23.90	134.2384	225.83	351.07

Where Ti = temperature ignitation, ti = ignitation time, Tb = temperature burnout, tb = burnout time

3.3Ignition and burn out performance

In this study, performance index was calculated from the value of combustion characteristics biopellet which aims to determine the impact of torrefaction on its combustion performance [3]. The ignition index (Di) is defined as the thermal probability of combustion at the initial stage which is determined by the amount of volatile compounds removed. Ignition index and burnout index are also determined to evaluate the reactivity of fuel combustion. The higher ignition index and burnout index, the more reactive fuel. To evaluate reactivity performance, the ignition index and burnout index is obtained from the following equation 2 and [3]:

The value of the ignition index raw EFB biopellet is 8.154×10^{-1} wt.% min^{-3} which then increases after the torrefaction process at temperatures 200°C, 250°C, dan 300°C to 5.203×10^{-1} wt.% min^{-3}, 3.959×10^{-1} wt.% min^{-3}, and 7.71×10^{-2} wt.% min^{-3}.

Higher ignition and burnout index values indicate that the fuel is more reactive. So, fuel is more flammable. Table 2. present that EFB biopellet after torrefaction is more difficult to burn, it can be advantageous in the biopellet storage process. Biopellet which has low reactivity is not burn easily when stored. The torrefaction process is able to improve the characteristics of biopellets as fuel.

In previous study [12] coal had an ignition index of 8.1×10^{-3} and EFB pellet after torrefaction at 300°C. It has value close to coal, which is 7.71×10^{-2} and a burn out index of 8.212×10^{-2}.

Table 2. Ignition index and burn out index

Sample of biopelet	di (wt.% min^{-3})	db (wt.% min^{-4})
EFB Raw	8.154×10^{-1}	1.1471
EFB 200 ℃	5.203×10^{-1}	7.907×10^{-1}
EFB 250 ℃	3.959×10^{-1}	5.831×10^{-1}
EFB 300 ℃	7.71×10^{-2}	8.212×10^{-2}
Cassava stem Raw	4.876×10^{-1}	8.154×10^{-1}
Cassava stem 200 ℃	4.113×10^{-1}	6.511×10^{-1}
Cassava stem 250 ℃	3.669×10^{-1}	6.014×10^{-1}
Cassava stem 300 ℃	2.815×10^{-1}	4.660×10^{-1}
Bagasse Raw	6.005×10^{-1}	9.063×10^{-1}
Bagasse 200 ℃	5.451×10^{-1}	8.405×10^{-1}
Bagasse 250 ℃	4.295×10^{-1}	6.435×10^{-1}
Bagasse 300 ℃	3.261×10^{-1}	4.961×10^{-1}
Napier Grass Raw	4.938×10^{-1}	8.328×10^{-1}
Napier Grass 200 ℃	3.996×10^{-1}	6.535×10^{-1}
Napier Grass 250 ℃	2.925×10^{-1}	4.831×10^{-1}
Napier Grass 300 ℃	2.891×10^{-1}	4.803×10^{-1}

4. Conclusion

Based on this study it can be concluded that torrefaction reduces ash content slightly and moisture content. The moisture content can affects the calorific value and ignitation. The decrease in moisture content in torrefaction biopellets are 2-5%, ash content are 1-5%, and volatiles are 8-14%. After torrefaction of biopellet, there was an increase fix carbon. The high fix carbon value affects the combustion, namely the biopellet is increasingly difficult to ignite. The fix carbon increase 3 times after torrefaction. The combustion rate of biopellet after torrefaction had decreased. This shows that the biopellet burns less per second, so then biopellet after torrefaction had longer burning time. The torrefaction process can also reduce the reactivity of ignition and burn out index, so that ignition and combustion temperatures are higher. Biopellet with low reactivity is not easy to flammable when storage. EFB biopellet torrefied at 300℃ had value close to low rank coal.

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