Coupled effect of torrefaction and densification pre-treatment on biomass energetic and physical properties

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Abstract: Leucaena *(Leucaena leucocepphala)* and oil palm empty fruit bunch, EFB *(Elaeis guineesis)* were selected as a woody and non-woody biomass samples, respectively in order to produce torrefied biomass pellets. In this study, torrefaction was performed at 300°C, three minute-residence time before pelletization. Then, the pellets have been characterized energetically and physically including volumetric energy density, and hygroscopic behavior. The results showed the torrefaction insignificantly enhanced high heating value of Leucaena from 19.3 MJ/kg to 19.5 MJ/kg and 18.3 MJ/kg to 19.1 MJ/kg for EFB. Moreover, torrefaction also improved the water resistance ability. While, the densification enhanced bulk density of biomass from 500 kg/m^3 to 527 kg/m^3 and 553 kg/m^3 to 574 kg/m^3 for Leucaena and EFB, respectively. The volumetric energy density was logically increased for both Leucaena and EFB biomass.

Keywords: Torrefaction, Densification, Biomass, Pellets.

1. Introduction

Biomass is an interesting choice to be one of the most important renewable energy sources. However, its nature is still not satisfied for most of the energy applications as it has high moisture content, low calorific value, and low bulk density. These drawbacks make high cost for storage and transportation of the biomass. Before to be use as biofuel, biomass has to be pretreated mechanically, physically, chemically or thermally.

Pre-treatment technology of biomass such as torrefaction and pelletization are very interesting to address the challenges [1]. Torrefaction is operated under an inert environment at 200-300°C, well-known as mild-pyrolysis which affects both physical and chemical property. In this temperature range, the biomass is completely dried and lost its fibrous structure [2]. Wei et al. [3] indicated that there are two major influences affecting mass and energy yields of the solid product in batch scale which are the torrefaction temperature and the type of biomass. During the torrefaction process, the three main structures of biomass including cellulose, hemicellulose, and lignin are decomposed. At the same time, the thermochemical decomposition also impacts hydroxyl functional group (-OH) displacement, making the torrefied biomass with new characteristics like water resistance property and biodegradation avoidance [4]. According to a previous study from Bergman and Kiel [5], torrefied biomass lost its tenacious structure which improve grindability and size reduction become more like coal. Moreover, other studies revealed that torrefaction improves fuel property. According to a typical mass-and energy balance of torrefaction process [6], it reviewed that at 70% mass remaining in a solid product could contain 90% of initial energy. Moreover, the torrefied biomass still has packing ability at this mass yield [7]. Moreover, torrefaction is able to increase calorific value and energy density by losing more hydrogen content and oxygen content, less carbon content in terms of condensable and non-condensable components [8].

As mentioned before, biomass has a low bulk density which make transportation and handling difficult. To face these drawbacks, thus, densification (pelletization) can solve this issue. The pelletization of biomass provides a mechanical force in order to pack biomass, makes a high volumetric density and more uniformity in shape and size of biomass [9].

The combination of these two technologies have been reviewed and studied to upgrade biomass becoming torrefied biomass pellets for energy conversion. Bergman [6] presented a Combined Torrefaction and Pelletization technology (The TOP process) for biomass upgrading as potential bio-pellets and indicated that this coupled process can improve the calorific value and the bulk density of feedstock. Furthermore, Kumar et al. [4] reviewed that there are two potential pathways to produce torrefied pellets including: upstream and downstream torrefaction/pelletization. Obviously, the upstream torrefaction/pelletization is an integration of torrefaction as an upstream unit or be operated before densification process. The downstream torrefaction/ pelletization is an integration of torrefaction as a downstream unit or be operated after densification process. An interesting result from Stelte reported that the torrefied biomass is more difficult to be compacted than raw biomass [9]. So, it is quite important to find the good conditions to produce pellets after torrefaction. Rudolfsson et al. [10] studied the effects of torrefaction and pelletization parameters on the quality of pellets. From torrefaction temperature, torrefaction time, moisture content (MC), and press channel length (PCL), the result indicated that torrefaction temperature is the greatest influence on the quality of pellets following by torrefaction time, MC, and PCL Furthermore, having longer PCL and higher MC give good quality of pellet.

In this study, the upstream torrefaction/pelletization integration was investigated at 300°C by using a horizontal vibrating reactor and a pellet mill to produce 25% mass loss torrefied Leucaena and EFB pellets. After that, the torrefied biomass pellets were studied the characteristics and properties between the untreated pellets (white pellets) and torrefied pellets (black pellets). The results from this study would provide the basic information for bio-pellets markets.

Table 1. Different particles size of the raw biomasses.

Biomass	Chips and fiber	8 mm particles size	< 250 µm particles size
Leucaena (Leu)			
Empty fruit bunch (EFB)			

2. Experimental section

2.1 Biomass preparation

Two different species of biomass were selected as samples for this study. Leucaena *(Leucaena leucocepphala)* was chosen as a woody biomass, provided by KWM Company. Empty fruit bunch oil palm *(Elaeis guineesis)* was chosen as a non-woody biomass, provided by Phoenix Pulp & Paper Public and Thachang companies. According to the different characteristics of these biomasses such as size, shape, and moistness, the raw materials were prepared to have similar characteristics before experiment. The biomasses were naturally dried and then forced dried in an oven before size reduction. They were cut and sieved into 8- and 2-mm particle size (RETSCH Model SM 2000) and ground to become powder ($< 250\,\mu$m). After that, the prepared raw materials were stored in an air-tight zipper bag before to be processing. The raw and prepared biomasses were shown in Table 1.

2.2 Characterizations of raw and torrefied biomass

The raw and torrefied biomass were analyzed in four basic characterizations which includes proximate analysis, ultimate analysis, gross calorific value, and ash element content using Thermogravimetric analysis (TGA), CHN elemental analyzer (J-Science JM10), calorific value calculation, and X-ray fluorescence (XRF), respectively.

2.2.1 Proximate analysis

The proximate analysis includes moisture content, volatile matter, fixed carbon and ash content of the sample by using a Thermal Gravimetric Analyzer (TGA), Shimudzu model TGA-50H. In the process, three different steps were performed: drying, devolatilization in an inert atmosphere (N_2), and combustion in oxygen (O_2). About 7-10 mg of the ground sample was heated from room temperature to 110°C with 10°C/min of heating rate, 50 ml/min of nitrogen flow rate and maintained for 10 minutes in order to quantify the moisture content. After that, the second step was heated up to 900°C with the same conditions to determine the volatile matter. At 900°C, the condition was changed into the air atmosphere in order to analyses the fixed carbon from losing weight and the ash content from the remaining solid.

2.2.2 Ultimate analysis

The ultimate analysis is an elemental content analysis which gives the percentage of the key element components in biomass such as carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) is calculated by difference. In this study, the Organic Elemental Analyzer (OEA) instrument used is an elemental analyzer (J-Science MICRO CORDER JM10). The ground materials were dried overnight at 70°C in the oven to remove moisture before analyzed. 2 milligrams of sample were loaded in the container to determine carbon, hydrogen, nitrogen, and sulfur in an excess oxygen condition. After the process, ash or remaining solid is an inorganic compound of a sample were input to calculate the result in dry-ash-basis.

2.2.3 Gross calorific value analysis

The gross calorific value (GCV) or High Heating Value (HHV) is an amount of heat from a complete combustion of sample including heat vaporization of the moistness in the sample and H_2O product from the reaction. In this study, the calorific value of biomass was calculated from a developed correlation using the percentage of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) from ultimate analysis as following equation [11-13]:

$$\text{HHV (MJ/kg)} = 0.3491\,C + 1.1783\,H + 0.1005\,S - 0.1034\,O - 0.0151\,N - 0.0211\,Ash$$

As Chen et al. [11] reviewed the developed correlations using proximate analysis, elemental content, or fiber content. Many correlations use fixed carbon, volatile matter, carbon, hydrogen, or lignin content as the main variable of calorific value estimation. For example, Channiwala and Parikh [12] presented the correlation of higher heating value (HHV) from elemental analysis of fuels an average absolute error of 1.45% and bias error as 0.00%. Moreover, REVE [13] also agreed with the HHV estimation using element composition in sample.

2.2.4 Ash elemental analysis

In this study, the XRF (X-ray fluorescence) was used to determine the elemental composition in ash of biomass sample. There are three elements were interesting in this study including Sodium (Na), Potassium (K), and Cl (Chloride) which are able to form an inorganic phase resulting in slagging or corrosion [14]. For ash preparation, 10 g of sample are combusted in muffle furnace at 575°C, 6 hours. Next, a few grams of ash sample were analyzed by Wavelength Dispersive X-ray Fluorescence (WD-XRF) with 34 mm. diameter for analytical area. The higher resolution of WDXRF provides reducing of spectral overlaps, so complex samples can be more accurately analyzed. Accordingly, the high-resolution backgrounds are reduced, providing improved detection limits and sensitivity of the instrument.

2.3 Torrefaction process

The torrefaction of biomass samples was investigated at 300°C in order to obtain 25% mass loss of biomass on dry basis.

The torrefaction behavior of each biomass at micro particle scale was studied by thermal gravimetric analyzer (TGA), Shimudzu model TGA-50H in order to figure out the holding time of torrefaction at 300°C. About 7-10 mg of the sample powder was heated under the nitrogen atmosphere from ambient room temperature to the desired temperature with 10°C/min of heating rate and hold at the final temperature around 30 minutes. In this process, residence time of torrefaction was considered at the desired mass loss on dry basis.

After that, the torrefaction process was performed by a pilot scale horizontal vibrating reactor. The schematic diagram of the reactor is shown in Fig. 1. For inert environment, 3 L/min of nitrogen flow rate was purged through the feeding tank. The reactor was heated up to reach the desired temperature. After that, the temperature was controlled in a range of 300 ± 10°C, meanwhile, the vibrating motors were working. When the temperature was constant, around 1000 grams of the prepared raw biomass were continuously feeding into the reactor for three minute-residence time. At the end of the process, the vibration, and nitrogen injection were still running to ensure that there is no

biomass in the reactor anymore and avoiding the condensation of tar in the reactor, respectively. Afterwards, the solid product was cool down in an inert condition to avoid the ignition with the contact of air. Then the solid product was weighted to calculate the weight yield and kept in the air-tight zipper bag before to be analyzed.

2.4 Pelletization process

This pelletization was conducted in batch scale by a flat die pellets mill. White and black pellets were produced from Leucaena and EFB. First, the material was mixed with 1-2 % of water without any additive to forms a liquid layer on the surface of the biomass particles and make lignin as a natural binder [15]. Next, the material was fed in front of a rolling press before to be pressed down into the die block (Fig. 2). The new material was continuously fed to the machine. The pellets were produced from the pellet mill with an approximately 8 mm in diameter, and about 30 mm in length. The process was repeated until all materials become in a pellet form. Afterwards, the pellets were dried in an oven for 24 hours to prevent bio-degradation.
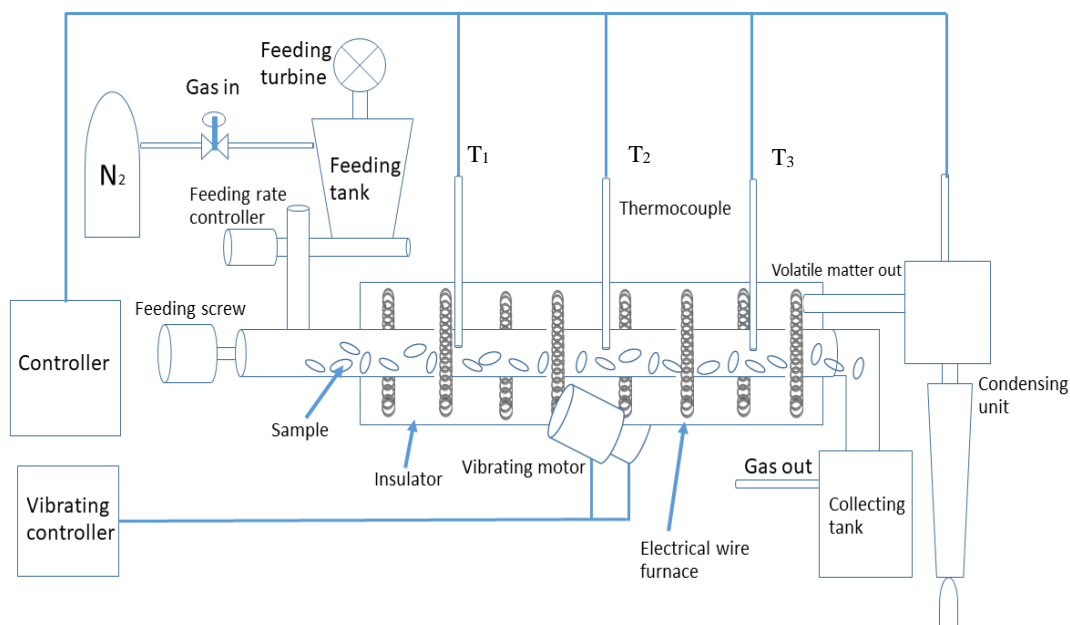

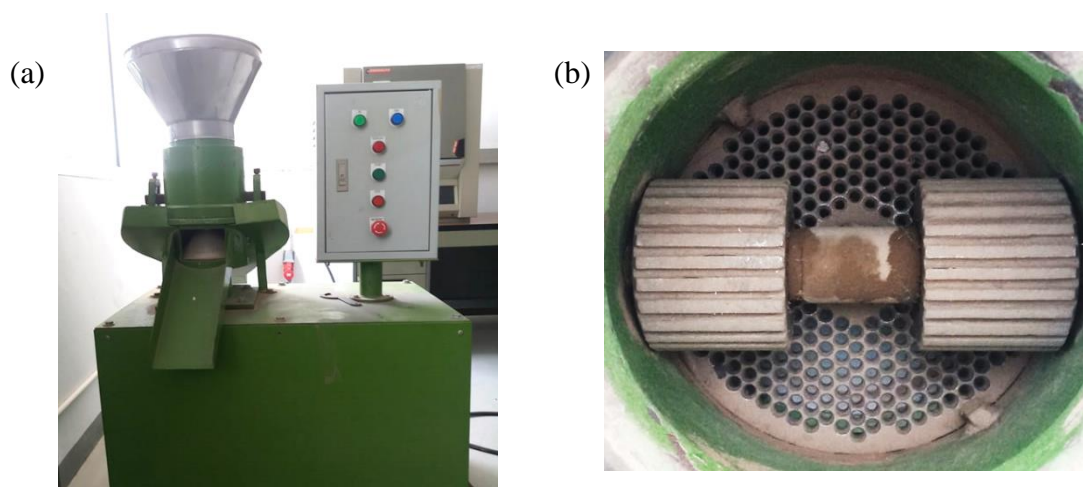**Figure 1.** Schematic diagram of the horizontal vibrating reactor.

Figure 2. (a) Pellet mill, (b) roller and pellet die blocks.

2.5 Raw and torrefied pellets characterization
2.5.1 Determination of a single pellet density

The basic dimensions of pellets were determined according to EN*plus* [16]. The EN*plus* was merged between European standard for wood pellets in 2011 (EN 14961-2) and the international standard (ISO 17225-2). It provides diameter, height, or thickness (mm) and length (mm) of wood pellets in groups. Ten pellets of each sample, both raw and torrefied were randomly picked to measure the density. They were cut into 2 mm in length in order to normalize the measurement. After that, the pellets were measured in diameter, length by the Vernier Caliper with a readability of 0.01 mm and weight by a laboratory balance with a readability of 0.0001 mm as piece by piece. The volume of each pellet was calculated as a normal geometric cylinder. Then, the single pellet density was determined an average value of the pellet.

2.5.2 Determination of bulk pellet density and volumetric energy density

The bulk density of pellets was determined by measuring the bulk volume and the weight of pellets. The bulk volume of pellets was performed by using one liter of a plastic measuring cylinder laboratory filling with sample pellets. After filling the pellets, the cylinder was patted on a table for three times to ensure the pellets were put on the right way. Then, only the pellets were weighted. The measurement was repeated three times. So, bulk density was calculated and averaged from the measurement. Then, the volumetric energy density is an energy value that the biomass carries in one unit of volume, mostly, (kJ/m^3). It is calculated by multiply heating value with bulk density.

2.5.3 Hygroscopic behavior

The equilibrium moisture content (EMC) was studied to examine the hygroscopic behavior of both raw and torrefied pellets at three different percentages of relative humidity (RH) as reviewed in Brachi et al.'s study [17]. The equilibrium relative humidity was performed by saturated salt solution of $MgCl_2$ (31.6% RH), NaCl (74.7% RH), and KCl (82.3% RH). The analytical grade of salt crystals was dissolved in deionized water at 40°C to prepare the salt solution. Moreover, solid salt crystals were added to make supersaturated salt solution and ensure the concentration theoretically remains constant. Then, the solution was contained in a glass chambers and kept at 40.0 ± 0.1°C in water bath to control environmental temperature. Three dried pellets were put in a small glass bottle and then weighed before placed in the chamber. Weight of pellets was measured in every day for 16 days. The equilibrium moisture content was calculated by following equation;

$$EMC\ (\%) = \frac{Wt - Wi}{Wi} * 100$$

Where Wi = initial weight of pellets
       Wt = weight at time of pellets

3. Results and Discussion

3.1 Characterizations of raw biomass

Proximate analysis, ultimate analysis, calorific value, and ash element content are presented in the Table 2. The TG curves are shown in the Fig. 3.

From the Fig. 3, the decreasing of the weight fraction can be observed. Volatile matter is the major component of both biomasses. Leucaena had 87 wt% of volatile matter, while, EFB had 78 wt% as shown in the no. 1 and 2. After introducing air, the sample was fully oxidized. Range no.3 and 4 in the figure showed fixed carbon of Leucaena and EFB with 12 wt% and 18 wt%, respectively. The last part was the solid remaining (ash) after combustion. The percentage of ash in EFB was significantly higher than Leucaena around 4 times. Normally, the ash content of wood depends on the mixture of bark content due to the minerals absorbed in that plantation area [14]. The ultimate analysis (Table 2) showed carbon and oxygen content were the major elements of biomass. Leucaena had the higher carbon content with 48 wt%. It will have an effect to the calorific value calculation of the feedstock, indeed that the high heating value of Leucaena was slightly higher than EFB. The element compositions of ash were also investigated. The result indicated that Potassium is the major ash element in both biomasses. Potassium content was significantly different between Leucaena and EFB which is 3,400 ppm and 17,800 ppm, respectively. Likewise, Chlorine content was 10 ppm in Leucaena, 7 ppm in EFB. While, Sodium content was insignificantly different in both biomasses. The results would be indicated fouling formation due to assembling of active alkaline (Na, K) with Sulfur oxide (SO_x) or Chlorine (Cl). Also, it is able to be a slagging when the active alkaline merges with oxide [18].

Table 2. Characterizations of raw Leucaena (Leu) and empty fruit bunch (EFB).

	Raw biomass	
	Leucaena	**Empty fruit bunch**
Proximate analysis (%wt, d.b.)		
Volatile matter	86.7	78.2
Fixed carbon	12.4	18.1
Ash	0.9	3.7
Ultimate analysis (%wt, d.b.)		
C	47.5	45.4
H	6.4	6.4
N	0.4	0.7
O (diff.)*	44.8	43.9
HHV (MJ/kg, d.b.)	19.4	18.7
Ash element (ppm)		
Na_2O**	77.0	143
K_2O	3,375	17,802
Cl	10.2	711

* By difference (O content was determined by $100 - (C + H + N + S)$).
** Na_2O, K_2O, and Cl refer to sodium (Na), potassium (K), and chloride (Cl), respectively

3.2 Study of pyrolysis behavior

Study of pyrolysis behavior in TGA of each biomass sample was conducted in order to understand the thermal degradation of biomass. The weight decreasing profile of both biomass samples were consider in temperature at 200-600°C. Fig. 4 shows TG curves and DTG curves of the biomass samples. The TG curves of all biomasses could be separated into three ranges which are 100-200°C, the biomass was completely dried, 200-400°C and 400-600°C, the biomass was disintegrated and released the volatile matter. It was found that the weight decreasing profile of biomass was rapidly decreased in the range no.2 (200-400°C). From DTG curves, they showed that weight of EFB started decreasing at 200°C. Otherwise, the weight of Leucaena started decreasing at 230°C. Moreover, the curves could be considered in two terms which are the temperature at maximum weight decreasing rate and the maximum weight decreasing rate. The temperature at maximum weight decreasing rate (T_{max}) indicates how reactive the sample is on the thermal reaction. While, the maximum weight decreasing rate indicates evaporation of the sample [19]. The figure presented that the maximum weight deceasing rate of EFB was the highest

almost 0.8 min^{-1} and occurred at the lowest temperature (at 330°C) following by weight decreasing rate of Leucaena around 0.6 min^{-1} which occurred around 360°C. At temperature higher than 380°C, the biomass was slowly disintegrated. The results could be concluded that EFB was easier decompose into vapor and more reactive on thermal decomposition than Leucaena. Nevertheless, the results were related to the chemical compositions in biomass: hemicellulose, cellulose and lignin which were decomposed around 200-600°C. It is well understood that the decomposition of biomass relies on physical composition, chemical composition, and chemical bond in the feedstock as well [20]. So, the results could be suggested that empty fruit bunch has higher amount of hemicellulose and cellulose as same as they were thermal decomposed easier than others following by Leucaena. So, at the torrefaction temperature range, it would be suggested that a cause of torrefaction sensitivity is due to the quantity of hemicellulose of biomass. Therefore, these results could be discussed that the EFB was more reactive in thermal decomposition at high temperature than Leucaena. However, a small amount of cellulose, lignin, and other organic compositions in biomass were also destroyed at this temperature range.
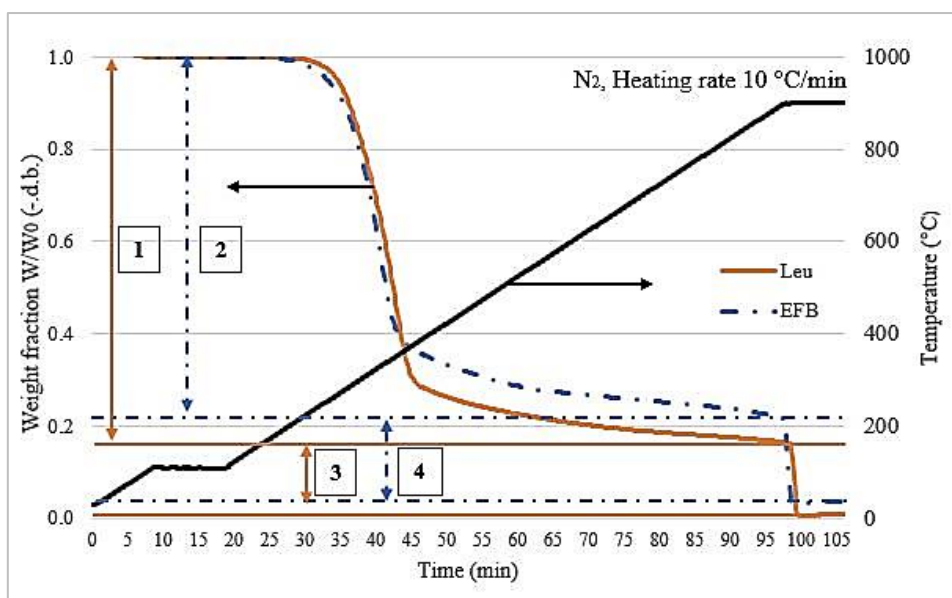

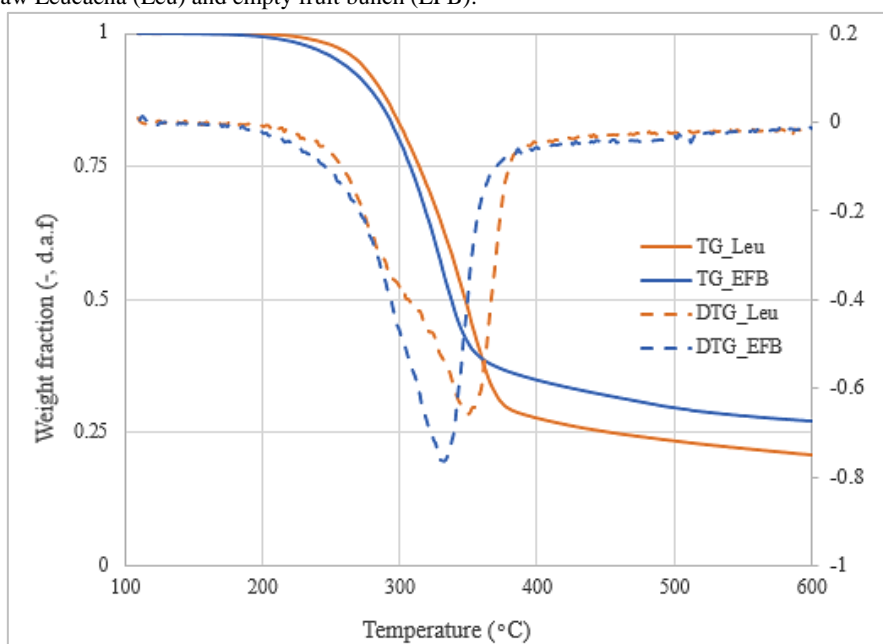**Figure 3.** TG curves of raw Leucaena (Leu) and empty fruit bunch (EFB).

Figure 4. TG curves and DTG curves of the biomass samples.

Table 4. Torrefaction conditions for 25±5% in mass loss (d.b.)

Biomass	Torrefaction conditions			Mass loss (%)
	Temperature (°C)	Feeding rate (kg/hr)	Residence time (min)	
Leucaena	300	1.5	3	22
Empty fruit bunch	295	1.0	3	21

Table 5. Characterizations of raw and torrefied Leucaena (Leu) and empty fruit bunch (EFB). d.b. = dry basis.

Sample	Proximate analysis (%, d.b.)			Ultimate analysis (%, d.b.)				HHV (MJ/kg, d.b.)	Solid yield (%, d.b.)
	VM	FC	Ash	C	H	N	O		
Raw_Leu	86.7	12.4	0.9	47.5	6.4	0.4	44.8	19.4	100
Tor_Leu	79.1	19.3	1.6	48.6	6.1	0.4	43.3	19.6	78
Raw_EFB	78.2	18.1	3.7	45.4	6.4	0.7	43.9	18.7	100
Tor_EFB	73.5	22.7	3.8	47.7	6.2	0.4	42.0	19.5	79
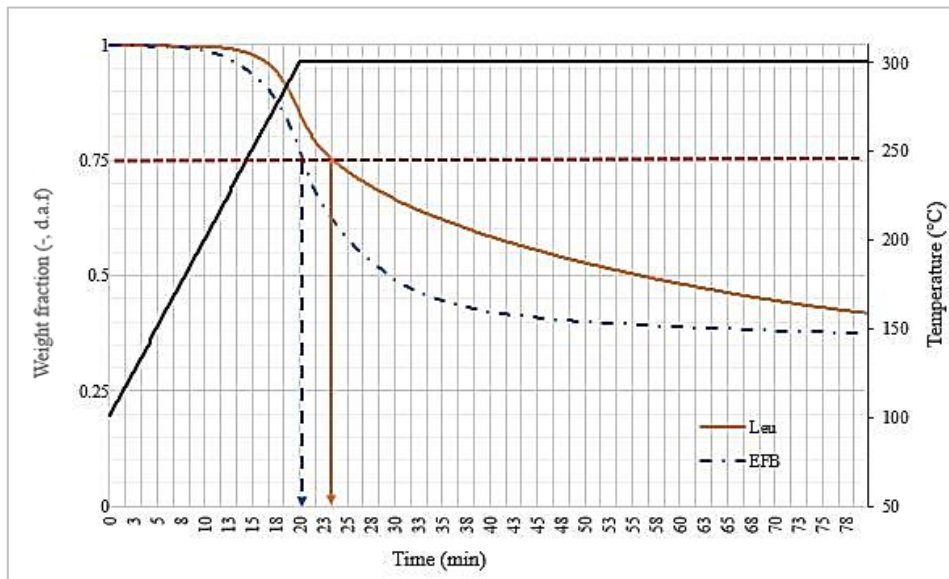
Figure 5. Investigation of holding time at 300°C by TGA for Leucaena (Leu) and empty fruit bunch (EFB).

3.3 Torrefaction process
3.3.1. Investigation the holding time of torrefaction

The investigation of holding time at 25% mass loss on dry basis of the feedtock samples was also conducted by TGA. Fig. 5 shows TG curve of biomass torrefaction at 300°C. It was performed in the same conditions as the study of pylorysis behavior. However, the sample was heat up to the desired temperature and hold for 30 minutes.

The weight loss behavior for both biomass samples was different. Empty fruit bunch mass started to decrease at 200°C and keep decreasing rapidly until 300°C. On the other hand, Leucaena weight loss started to decrease at 250°C and keep decreasing rapidly. The residence time was considered when the temperature was heat up to 300°C at the 25% mass loss of biomass. The TG curve showed that EFB doesn't need holding time to loss its 25% mass. While, Leucaena needs three minute-holding time after 300°C. These results can be confirmed by study of pyrolysis behavior that bio-structure of EFB was degraded easier than Leucaena at lower temperature. It also would be an effect from the compositions of biomass. At this torrefaction temperature, the hemicellulose in biomass was degraded. The losing weight consisted of H_2O, CO_2, and CO in gaseous form and condensable components [21].

Table 3. Residence time of torrefaction (min) at 25% weight loss of the biomass by using TGA.

Biomass	Residence time (min)
Leucaena	3
Empty fruit bunch	0

3.3.2. Torrefaction process

The torrefaction was firstly conducted in a horizontal vibrating reactor in order to obtain the 25% in mass loss on dry basis of Leucaena and empty fruit bunch. Table 4 shows the torrefaction conditions and percentage of mass loss of the samples. According to the study of pyrolysis behavior and investigation of holding time in TGA, it was found that EFB is very sensitive at high temperature. So, at 300°C and 295°C with three minute-residence time were condition for torrefaction of Leucaena and EFB. The torrefaction conditions gave a 22% and a 21% mass loss for Leucaena and EFB, respectively.

Table 4 shows the torrefaction conditions and percentage of mass loss of the samples. The results revealed that, at similar torrefaction conditions (~300°C, 3 min), the torrefied Leucaena and EFB remained weight at 22% and 21% on dry basis, respectively. According to the previous study in pyrolysis behavior, it was found that empty fruit bunch was very sensitive at the desired temperature. In addition, using the vibrating reactor, temperature is one of conditions of the process. So, empty fruit bunch was reduced the setting temperature from 300°C to 295°C which was acceptable in range 300±10°C, as mentioned in methodology. These results also indicate that torrefaction conditions in the continuous and moving system (vibrating reactor) are unique and individual in each type of biomass.

3.4 Characterizations of raw and torrefied biomass

Proximate analysis, ultimate analysis, calorific value, and ash element content of raw and torrefied biomass are presented in

Table 5. The proximate analysis of each sample was calculated by thermogravimetric analysis (Fig. 6). The ultimate analysis shows the percentage of major elements in biomass which used to calculate the calorific value of the samples.

Fig. 6 shows that the volatile matters are still the major components in both raw and torrefied biomass. According to the Table 6, the results also indicated that volatile matter and oxygen content from the torrefied biomass were decreased (from 87 wt% to 79 wt% for Leucaena and 78 wt% to 74 wt% for EFB) and (45% to 43% for Leucaena and 44% to 42% for EFB, respectively). On the other hand, the fixed carbon as well as carbon content was increased in torrefied biomass (from 12 wt% to 19 wt% for Leucaena and 18 wt% to 23 wt% for EFB) and (48% to 49% for Leucaena and 45% to 48% for EFB), respectively. The nitrogen and hydrogen content were insignificantly different which was around 6% and 0.4 %, respectively. According to these results, it was confirmed that torrefaction process has changed the chemical composition of feedstock. Wannapeera & Worasuwannarak [22] and Wei et al. [3], that during the torrefaction, hydroxyl groups in

biomass were destroyed to become condensable and non-condensable matters. They were decomposed in the form of H_2O, CO_2, CO, and acetic acid. Interestingly, at the very similar yield of solid product, the increasing of carbon content in EFB was significantly higher than Leucaena which affect to the increasing a bit of calorific value of both samples. However, Leucaena still has more calorific value than EFB. The percentage of ash content was increased when decreased the solid mass concentrating the inorganic compounds in biomass, becoming the remaining solid after combustion.

3.5 Properties of raw and torrefied pellets
3.5.1 Pellet density

Both raw and torrefied biomass samples were pelletized in order to study their density. Table 6 shows the physical apparence of untreated and torrefied pellets. As expected, the color of torrefied pellets in both leucaena and EFB were darker than their raw pellets. Therefore, raw biomass pellets were called white pellets, while, torrefied biomass pellets were called black pellets.
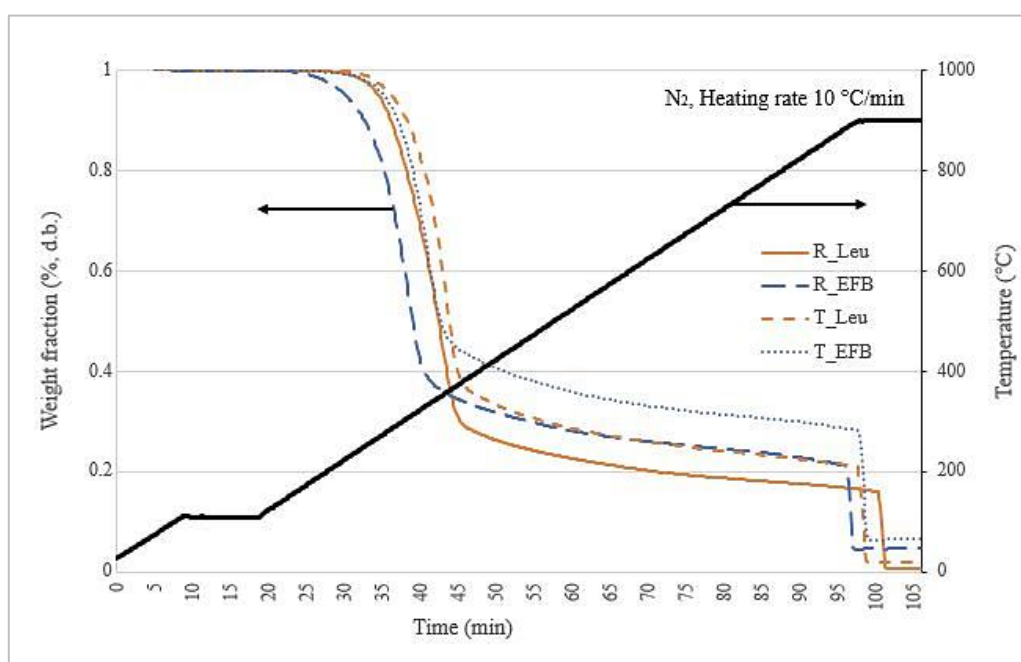

Figure 6. TG curves of raw (R) and torrefied (T) Leucaena (Leu) and empty fruit bunch (EFB).

Table 6. Raw and torrefied pellets of leucaena and empty fruit bunch.

Biomass	Raw pellets	Torrefied pellets
Leucaena (Leu)		
Empty fruit bunch (EFB)		

Table 7. Characterizations of raw and torrefied Leucaena (Leu) and empty fruit bunch (EFB).

Sample	Diameter (mm)	Length (mm)	Density (kg/m³)		Vol. E_d (GJ/m³)
			Pellet	Bulk	
Raw_Leu	7.7	22.0	1,215.5	500.5	9.7
Torrefied_Leu	7.9	21.4	1,209.3	527.4	10.3
Raw_EFB	7.8	20.7	1,176.2	552.8	10.3
Torrefied_EFB	7.9	21.6	1,210.6	574.2	11.1
EN*plus*	6±1 or 8±1	3.15<L≤40*	Not required	600≤BD≤750	Not required

*a maximum of 1% of the pellets may be longer than 40mm, no pellets longer than 45mm are allowed

Table 7 presents the pellet density of raw and torrefied bio-pellets compare with the European standard (EN*plus*). The results showed that diameter and length of these pellets were similar with 7.7-7.9 mm and 20.0-22.0 mm, respectively. The diameter and length of the produced pellets were also in range of the EN*plus*. It was clearly seen that a single pellet and bulk density of torrefied biomass of leucaena and EFB are higher than the raw biomass. One of the reason might be the improvement of the grindability of torrefied biomass due to the lost of its fibrous structure making easier the packing of torrefied biomass compared to the the raw.

One of interesting property of biomass pellets is volumetric energy density. It was estimated by the following equation:

Volumetric energy density (Vol. E_d, GJ/m³) = $Bulk\ density\ (kg/m^3)\ x\ HHV\ (GJ/kg)$

According to the Table 7, it could be discussed that the increasing of volumetric energy density of torrefied bio-pellets is a consequence of torrefaction and pelletization. As mentioned, the torrefaction can improve the high heating value of biomass and the pelletization can improve the bulk density of biomass. The volumetric energy density of torrefied Leucaena increased from raw to torrefied, (9.7 to 10.3 GJ/m³). While, the volumetric energy density of empty fruit bunch increased from raw to torrefied, 10.3 to 11.1 GJ/m³, respectively. A review from Kumar 2016 [4] revealed that volumetric energy density of wood pellets and torrefied pellets is in range between 8-11 GJ/m³ and 15-18 GJ/m³. However, it could be discussed that the produced pellets which remaining 25±5% mass loss in torrefied biomass with high temperature, short residence time did not significantly enhance the energy content of biomass. The bulk density of torrefied biomass also was not qualified. Therefore, it could be suggested proper pelletization conditions should be investigated for quality of packing or technological pellet mill should be performed.

3.5.2 Hygroscopic behavior
The equilibrium moisture content (EMC) in different relative humidity was measured to study the hygroscopic or moisture uptake behavior of the raw and torrefied pellets of Leucaena and empty fruit bunch. The EMC of bio-pellets was studies in three different environments including 31.6%, 74.7%, and 82.3% RH. The moisture uptake behavior of both Leucaena and empty fruit bunch were first investigated. Fig. 7 and Fig. 8 show the percentage of moisture content of raw and torrefied biomass. From both figures, the complete lines represent the white pellets, and the dashed lines represent the black pellets. While, the circle, triangle, and square points on the line show the relative humidity which is 31.6%, 74.7%, and 82.3% RH, respectively.

According to the Figs. 7 and 8, it can be seen that pellets in high relative humidity (82.3% RH) absorbed more water compared to the lower humidity (74.7%, 31.6% RH). Moreover, the torrefied pellets in both biomasses presented less moisture content than their respective raw pellets. However, the trend of moisture content increased is similar in both raw and torrefied samples. All of pellet samples pellets absorbed a lot of water in the first two days and become steadier at day 6. Fig. 9 shows the final weight (day 16) of the bio-pellets at the three-relative humidity.

The results showed that raw and torrefied Leucaena pellets absorbed a lower amount of water compared to EFB. The suggestion would be confirmed by the oxygen content in hydroxyl groups in raw and torrefied Leucaena were lower than EFB. Indeed, it is well known that the hydroxyl groups are involved in the hygroscopic property of biomass [11]. So, the torrefied EFB pellets becomes more hydrophobic than torrefied Leucaena pellets. Therefore, these results could be suggested that torrefaction can enhance the hydrophobicity of the pellets. Influentially, these results would be beneficial for pellets' storage in open area mixed with coal. The better water resistance property in torrefied bio-pellets can avoid the biological degradation (i.e. fungal and bacteria) [1, 9, 11].

4. Conclusion

Torrefaction is a well-known pretreatment of biomass at 200-300 degree Celsius in an inert environment. It has been studying in order to enhance properties of biomass for example calorific value and hygroscopic behavior. Densification is also well-known and widely used by providing a mechanical force to pack biomass. The technique makes high volumetric density and uniformity in shape and size of biomass. So, the combination of torrefaction and densification was interesting in order to express the potential biomass. In this study, Leucaena *(Leucaena leucocepphala)* and oil palm empty fruit bunch *(EFB, Elaeis guineesis)* were selected as a woody and non-woody biomass sample. Pyrolysis behavior of each biomass sample was studied. It indicated that EFB is more sensitive than Leucaena at 300°C. Then, the samples were studied their residence time of torrefaction by TGA at the desired temperature with 10°C/min of heating rate. Expectedly, EFB needs no residence time to get 25% mass loss, while, Leucaena needs three minutes for holding time.

Leucaena and empty fruit bunch, were torrefied at 300 and 295°C, respectively with three-minute residence time in nitrogen atmosphere. At this torrefaction temperature, Leucaena lost 22 wt%, while, EFB lost 21 wt%. It affected to oxygen and carbon content in torrefied biomass. The oxygen content was decreased, otherwise, carbon content was increased which is a cause for increasing high heating value of torrefied biomass samples. The high heating value of both Leucaena and EFB slightly increase. Moreover, the color of the samples turned to be darker than untreated biomass.

After that, the torrefied samples were densified by a pellet mill to produce the torrefied bio-pellets. The results showed that a single pellet and bulk pellet density of torrefied pellets was higher than the raw pellets. Then, the properties of pellets were studied. The volumetric energy density of biomass pellets was increased from raw to torrefied pellet around 6% and 8% for Leucaena and empty fruit bunch, respectively. The hygroscopic property was revealed that the equilibrium moisture content (EMC) of torrefied Leucaena and empty fruit bunch were lower than the raw pellets.

Therefore, the coupled torrefaction and pelletization can improve the energetic and physical properties of biomass. Furthermore, this study ensures that the torrefaction and pelletization can address the challenges of biomass and turn the biomass become a high potential solid biofuel for industrial and domestic applications by improving the pellets' quality.
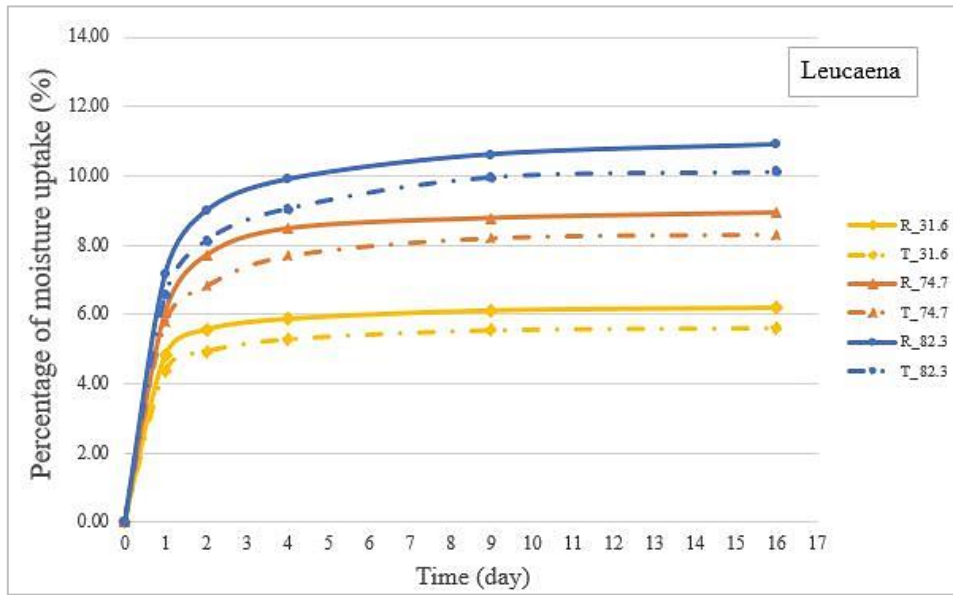
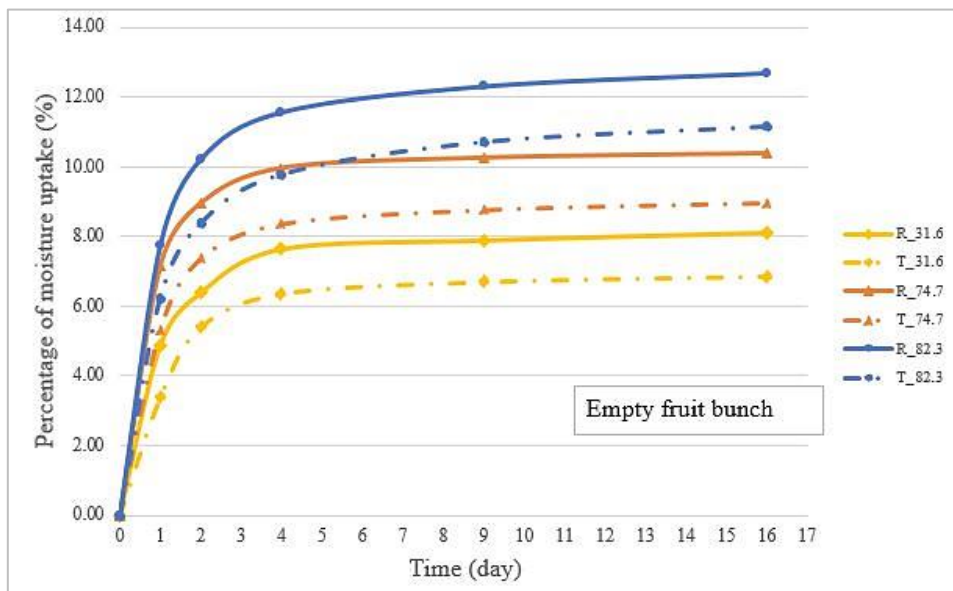**Figure 7.** Percentage of moisture uptake in raw and torrefied leucaena pellets.

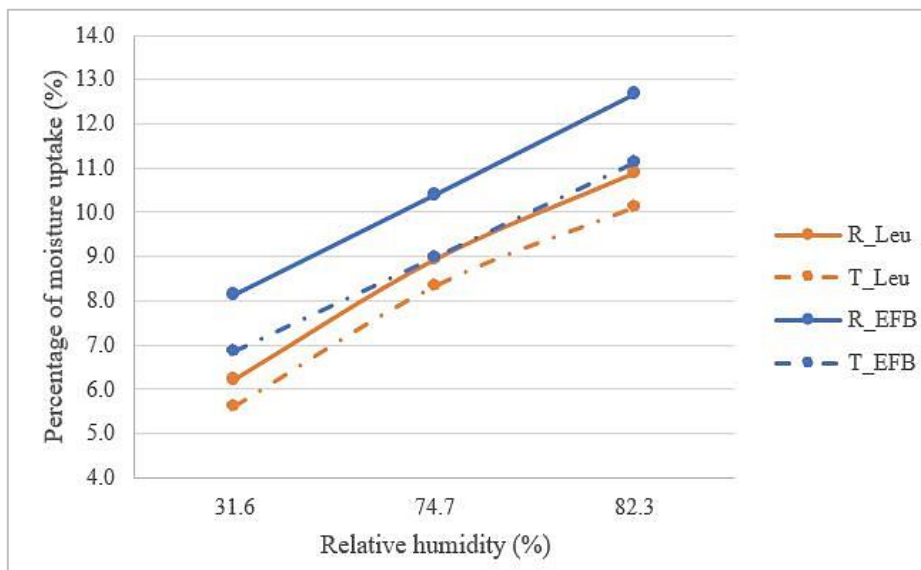**Figure 8.** Percentage of moisture uptake in raw and torrefied empty fruit bunch pellets.

Figure 9. EMC comparison between raw (R) and torrefied (T) leucaena and EFB pellets.

Acknowledgements

References

[1] Chew, J.J. and Doshi, V. 2011. Recent advances in biomass pretreatment – Torrefaction fundamentals and technology, *Renewable and Sustainable Energy Reviews*, 15(8), 4212-4222, doi: 10.1016/j.rser.2011.09.017.

[2] Fonseca Felfli, F., Luengo, C., Suarez, J. and Beaton, P. 2005. Wood Briquette Torrefaction, *Energy for Sustainable Development*, 9, 19-22.

[3] Wei, L., Gao, Y., Qu, W., Zhao, X. and Cheng, S. 2016. Torrefaction of raw and blended corn stover, switchgrass, and prairie grass, *Transactions of the ASABE*, 59(2), 717-726.

[4] Kumar, L., Koukoulas, A.A., Mani, S. and Satyavolu, J. 2016. Integrating Torrefaction in the Wood Pellet Industry: A Critical Review, *Energy & Fuels*, 31(1), 37-54, doi: 10.1021/acs.energyfuels.6b02803.

[5] Bergman, P.C.A. and Kiel, J.H.A. 2005. *Torrefaction for biomass upgrading*, ECN report, ECN-RX—05-180.

[6] Bergman, P.C. 2005. *Combined torrefaction and pelletization*, The TOP process (Rep. No. ECN-C--05-073), ECN biomass.

[7] Doassans-Carrère, N., Muller, S. and Mitzkat, M. 2015. REVE: Versatile Continuous Pre/Post-Torrefaction Unit for Pellets Production, In: *World Sustainable Energy Days Next 2014* (pp. 163-170) Chapter: Part II, Publisher: Springer Fachmedien Wiesbaden, Editors: Gerhard Dell, Christiane Egger, doi: 10.1007/978-3-658-04355-1_20.

[8] Chen, Y.-C., Chen, W.-H., Lin, B.-J., Chang, J.-S. and Ong, H.C. 2017. Fuel Property Variation of Biomass Undergoing Torrefaction, *Energy Procedia*, 105, 108-112. doi: 10.1016/j.egypro.2017.03.287

[9] Stelte, W. 2012. *Guideline: Densification of torrefied biomass*, Resultat Kontrakt (RK) Report, Energy & Climate Centre for Renewable Energy and Transport Section for Biomass.

[10] Rudolfsson, M., Borén, E., Pommer, L., Nordin, A. and Lestander, T.A. 2017. Combined effects of torrefaction and pelletization parameters on the quality of pellets produced from torrefied biomass, *Applied Energy*, 191, 414-424, doi: 10.1016/j.apenergy.2017.01.035.

[11] Chen, W.-H., Peng, J. and Bi, X. T. 2015. A state-of-the-art review of biomass torrefaction, densification and applications, *Renewable and Sustainable Energy Reviews*, 44, 847-866, doi: 10.1016/j.rser.2014.12.039.

[12] Channiwala, S.A. and Parikh, P.P. 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel*, 81(8), 1051-1063, doi: https://doi.org/10.1016/S0016-2361(01)00131-4.

[13] Doassans-Carrère, N., Muller, S. and Mitzkat, M. 2014. REVE — a new industrial technology for biomass torrefaction: pilot studies, *Fuel Processing Technology*, 126, 155-162, doi: 10.1016/j.fuproc.2014.04.026.

[14] James, A., Thring, R., Helle, S. and Ghuman, H. 2012. Ash Management Review-Applications of Biomass Bottom Ash, *Energies*, 5, 3856-3873.

[15] Hansen, M.T., Jein, A.R., Hayes, S. and Bateman, P. 2009. *English Handbook for Wood Pellet Combustion*, Available online: https://pelletsatlas.info/pellet-handbook-tool/english-handbook [Accessed 23 April 2018].

[16] European Pellet Council. 2015. Part 3: Pellet Quality Requirements, In *ENplus Handbook* (pp. 1-10). Brussels, Belgium: European Pellet Council (EPC).

[17] Brachi, P., Chirone, R., Miccio, M. and Ruoppolo, G. 2018. Fluidized Bed Torrefaction of Commercial Wood Pellets: Process Performance and Solid Product Quality, *Energy & Fuels*, 32(9), 9459-9469, doi: 10.1021/acs.energyfuels.8b01519.

[18] Singchai, A. 2008. *Study on the Probability of Slagging and Fouling Formation from Biomass by Physico-Chemical Method* (Unpublished master's thesis, 2008), Thammasat University.

[19] Choobuathong, N. 2007. *Effects of chemical composition of biomass on pyrolysis and combustion*, Master Thesis, Science, Chulalongkorn University.

[20] Wattananoi, W., Khumsak, O. and Worasuwannarak, N. 2011. Upgrading of biomass by torrefaction and densification process. Paper presented at the 2011 IEEE Conference on Clean Energy and Technology (CET), 27-29 June 2011.

[21] Wannapeera, J., Fungtammasan, B. and Worasuwannarak, N. 2011. Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass, *Journal of Analytical and Applied Pyrolysis*, 92(1), 99-105, doi: https://doi.org/10.1016/j.jaap.2011.04.010

[22] Wannapeera, J. and Worasuwannarak, N. 2015. Examinations of chemical properties and pyrolysis behaviors of torrefied woody biomass prepared at the same torrefaction mass yields, *Journal of Analytical and Applied Pyrolysis*, 115, 279-287, doi: https://doi.org/10.1016/j.jaap.2015.08.007.