Torrefaction of palm kernel shell using COMB method and its physicochemical properties

Karelius1*, M Dirgantara2, N Rumbang3, K G Suastika2, A R M Akbar4
1Department of Chemistry, University of Palangka Raya, Indonesia
2Department of Physics, University of Palangka Raya, Indonesia
3Department of Agriculture Cultivation, University of Palangka Raya, Indonesia
4Study Program of Agricultural Industry Technology, Lambung Mangkurat University, Indonesia

*karelius@chem.upr.ac.id

Abstract. Torrefaction is a pre-treatment in thermochemical processes in order to make biomass becomes fuel with better properties, such as the increasing of carbon content and caloric value. Torrefaction is generally carried out at a temperature range of 200-300°C with holding temperature of 30-60 minutes in inert conditions and atmospheric pressure. On the other side, palm oil is one of biomass that is potential to be used as fuel in which its availability is abundant and has good physical properties. The purpose of this study is to increase the caloric value and thermochemical properties by torrefaction process. Within this study of palm kernel shell, torrefaction is carried out from 0.5 cm sieve using the COMB (Counter Flow Multi-Baffle) method at temperature of 250 °C with heat flow rate of 4 cm³/minute and characterized by its physicochemical properties. The obtained results are the energy yield of 0.77 with an energy density of 1.21 and the caloric value that increases from 16.82 to 19.11 MJ. This is also supported by the results of ultimate analysis where the carbon level increases then the O/C and H/C ratio decreases. Moreover, based on proximate analysis, volatiles matter level decreases by 9.34% and ash content increases by 0.64%. To sum up, palm kernel shells can be enhanced by their physicochemical characteristics through torrefaction.

1. Introduction
Lignocellulosic biomass is one of the most important renewable energy resources. As a fuel, the raw material has several disadvantages, such as high oxygen content, low calorific value, low energy density, hydrophilic nature, and high moisture content [1]. One of the large biomass potentials in Indonesia is a by-product of the oil palm industry such as palm kernel shells and empty fruit bunches. The production of palm oil in Indonesia has always increased every year. It was 26 million tons in 2012 to 40.5 million tons in 2018 [2]. From this production, the biomass produced from the palm oil industry includes empty fruit bunches (23%), mesocarp fibers (12%) and palm kernel shells (5%) from every ton of fresh fruit bunches [3], [4]. The potential for that large biomass is a big loss if it is not utilized properly. So far many palm kernel shells have been exported to developed countries such as Japan to be used as fuel, but by exporting biomass it also exports the nutrients in it. Therefore, it is important to use palm kernel shells around the area of origin and later it will be returned to maintain soil fertility.

The thermochemical process of torrefaction is actually an incomplete pyrolysis process also known as mild pyrolysis, which is another widely applied and studied technology to increase the energy density of biomass and reduce the transportation and storage cost of biomass [5], [6]. Torrefaction occurs when
thermal heat is carefully applied to biomass under controlled thermodynamic conditions causing chemical, physical and mechanical changes to the biomass [7]. The temperature range required is between 200 and 300 °C and the process should occur under inert conditions, at low heating rates and low residence time[3], [8], [9]. Torrefied biomass retains most of its chemical energy and can be grinded easily in comparison to the raw biomass. In addition, torrefied biomass has increased uniformity with respect to product quality in terms of physical and chemical properties [9], [10]. One of the latest torrefaction methods developed by the Korea Institute of Energy Research (KIER) is biomass faction using counter flow multi-baffle (COMB) technology which currently also exists in Indonesia precisely at Lampung University. This technology has the advantage of low gas to solid ratio (G/S), short residence time (~ 5 min), constant difference (driving force) temperature along the column, simple, flexible & movable [11].

Currently, torrefaction process uses a batch method which takes 30-60 minutes, in this study COMB method will be used which has the advantage of a short torrefaction time of less than 5 minutes. The use of palm kernel shells into fuel through a torrefaction process to improve physicochemical properties can be a solution in maximizing biomass potential. In this research, the palm kernel shell shelling process was carried out with a size that passed the 0.5 cm sieve using the COMB method at a temperature of 250°C and a flowrate of 4 cm³/ minute. Shells before and after torrefaction then analyzed the efficiency process, calorie, ultimate and proximate parameters to determine their ability as fuel.

2. Method

2.1. Raw Material Preparation and Torrefaction

The raw material of palm kernel shell is obtained from palm oil production, sieved with a size of 0.5 cm and then dried in the sun to a moisture content below 9% so the fungus can not be grown and stored in an airtight bag to look for airborne levels remain stable [3], [12].

The torrefaction process was carried out at the Integrated Agriculture Laboratory, Tropical Biomass Research, and Development Center, Lampung University. Previous research has shown that at a temperature of 300 °C there is a high increase in calories in biomass; there will be a large mass loss for the process. At a temperature of 200 °C, the increase in calorific value is not significant, the temperature of 250 °C becomes the optimum temperature for the biomass faction process such as pine wood and corn cobs [13]. The torrefaction process carried out in this study using palm shell biomass with particle size passed 0.5 cm sieve, at a temperature of 250 °C with a heat flow rate of 4 cm³/ minute.

2.2. Analysis Proximate and Ultimate

Proximate analysis to determine ash content, volatile matter, and moisture content in this study was tested by using the gravimetric method with successive standards EN 14775: 2009, ASTM D 5142-02 and EN 14774-2: 2009. The ultimate test was done using the TruSpec CHN tool from Leco Inc. based on ASTM D 5373-16 standards (to determine the composition of carbon, hydrogen, and nitrogen). The proximate and ultimate analysis was carried out on samples before treatment and after the torrefaction process. [12], [14]

2.3. High heating value (HHV) Analysis

Measurements of calorific values was carried out to determine Higher Heating Value (HHV). These measurements were carried out by following the EN 14918: 2009 procedure using 6400 Automatic Isoperibol Calorimeters from Paar Instrument Company [14], [15]. The measured sample is sample before treatment and after the torrefaction process.

2.4. Parameter Efficiency Process

The four parameters that are very important to be used to determine the success of the torrefaction process are weight loss, mass yield, energy yield, and energy density. Focusing on the torrefaction process is to get a high HHV value and low mass loss due to this process [3], [12], [15].

1. Weight loss is calculated using the following equation
\[ \text{Weight loss (WH)} = \frac{M_i - M_t}{M_i} \]  
(1)

Where \( M_i \) is mass before torrefaction and \( M_t \) is mass after torrefaction process.

2. **Mass yield** is calculated using the following equation

\[ \text{Mass Yield (MY)} = \frac{M_t}{M_i} \times 100\% \]  
(2)

3. **Energy yield** is calculated using the following equation

\[ \text{Energy Yield (EY)} = MY \times \frac{CV_t}{CV_p} \]  
(3)

Where \( CV_t \) dan \( CV_p \) is the calorific value of shell after and before the torrefaction process.

4. Energy density is calculated using the following equations

\[ \text{Energy Densitas (DE)} = \frac{EY}{MY} \]  
(4)

### 3. Results and Discussions

#### 3.1. Torrefaction experiment

The torrefaction process was carried out at the Integrated Agriculture Laboratory, Tropical Biomass Research, and Development Center, Lampung University. The series of torrefaction devices is shown in Figure 1.

**Figure 1.** Torrefaction Equipments [11]

The results before and after the palm shell torrefaction with particle size passed 0.5 cm sieve, at a temperature of 250 \(^\circ\)C with a hot air flow rate of 4 cm\(^3\) / minute as shown in Figure 2.

**Figure 2.** (A) control shell; (B) Torrefaction shell; (C) Palm fiber [16]

One indicator of the success of the torrefaction process is the change in the physical appearance of biomass. In this case, the palm kernel shell. Figure 2 (B), showing different physical appearance colors on the palm shell after torrefaction becomes darker than the control shell (Figure 2 (A)). This is due to the carbonization process and the reduction of water content during torrefaction resulting in the color of the shell becoming darker [15]. In addition to the carbonization process, it turns out the torrefaction process with the working principle COMB can also separate fibers/litter from the palm shell (Figure 2 (C)) so that it no longer requires mechanical/manual separation.
3.2. Ultimate analysis
One of the parameters tested for the control shell and the torrefaction shell is the ultimate test. The ultimate test carried out is the determination of carbon content, hydrogen content, nitrogen, and oxygen levels. The test results can be seen in Table 1.

| Sample          | Carbon (%) | Hydrogen (%) | Nitrogen (%) | Oxygen (%) |
|-----------------|------------|--------------|--------------|------------|
| Control Shell   | 36.69      | 3.74         | 0.42         | 47.40      |
| Torrefied Shell | 46.73      | 4.37         | 0.39         | 43.51      |

Table 1 shows that the torrefaction process causes changes in the levels of carbon, hydrogen, nitrogen, and oxygen. The actual torrefaction process is a combustion process in a state of minimal oxygen [3], [17], it is hoped that not all shells that are extracted change into CO2 and H2O vapors. The combustion process under these conditions at a temperature of 200-300 °C causes carbonization events (increased carbon content) [18], although it still produces CO2 and H2O due to the availability of oxygen even in small amounts.

The results of the analysis showed an increase in carbon and hydrogen levels, as well as a decrease in the levels of nitrogen and oxygen in torrefaction palm kernel shells. Hydrogen and oxygen as one of the main components of biomass are one of the most lost components during the torrefaction process. Oxygen is the main component of the composition of volatile compounds which in the range 200 - 300 °C produces more phenol. While hydrogen is the main component of constituent liquid smoke (condensate) from the torrefaction process. Reduced levels of hydrogen and oxygen result in lower levels of volatiles and increase the ratio of carbon to hydrogen and oxygen [19]. The O/C ratio is very influential on the calorific value of a material, where the reduction of the O/C ratio results in an increase in calorific value [16]. Fuel with a high O/C ratio that has relatively high chemical energy will reduce gasification efficiency because with a high O/C ratio there is excessive oxidation so that the torrefaction process can reduce the O/C ratio. This happens because the torrefaction process occurs carbonization which causes the percentage of carbon and hydrogen content to increase, and the oxygen content decreases due to the combustion process so that through the torrefaction process it is very important to increase the calorific value of palm kernel shells.

3.3. Proximate analysis
The results of the analysis of the calorific value of each control shell and torrefaction shell are shown in Table 2.

| Sample          | Moisture (%) | Ash levels (%) | VM (%) |
|-----------------|--------------|----------------|--------|
| Control Shell   | 11.75        | 7.73           | 74.15  |
| Torrefaction Shell | 5           | 8.37           | 64.81  |

Based on the results of the proximate analysis, the torrefaction process can reduce the moisture of the palm shell by up to 5%. This shows that with torrefaction carried out at a temperature of 250 °C with a heat flow rate of 4 cm3 / minute, it can reduce moisture significantly. Moisture is one of the important factors for solid fuel, where high water content can cause a lot of energy loss in the combustion process due to the heat needed for the release of water from biomass [20]. Low moisture from the torrefaction process is expected to reduce the possibility of fermentation which can cause an increase in shell temperature, and reduce the risk of shell fire during storage in a long time.

The decrease in moisture and volatile levels is caused by the increasing amount of water and volatile components that evaporate, where volatile substances formed are polymers of hemicellulose which are degraded during the torrefaction process [18], [21]. Ash is the residual inorganic solid formed when biomass burns completely with its main composition, namely silica, aluminum, iron, calcium, and a
small amount of magnesium, titanium, and potassium [20], [22]. Small ash levels play a very important role in the thermal conversion of biomass, especially when biomass contains potassium or halides such as chlorine. These compounds can cause corrosion in the biomass processing gasification unit [22]. The ash content in palm shell torrefaction products increased after the torrefaction process. The increase in ash content in torrefaction products is due to the mass reduction that occurs during the torrefaction process is not accompanied by the degradation of the inorganic forming components.

3.4. High heating value (HHV)
HHV is the most important characteristic in terms of energy, especially in the combustion process to be able to produce energy that is compatible with other materials such as coal. HHV value is obtained in two ways, namely, direct analysis using 6400 Automatic Isoperibol Calorimeter with cal/gram unit which is then converted to MJ/Kg, and through comparison with calculation using carbon (C), hydrogen (H) and oxygen (O) content using the equation Chang Dong and Azevedo [23] as presented in Table 3.

\[
HHV(MJ/Kg) = -1.3675 + 0.3137C + 0.7009H + 0.0318O
\]

Where: C = percentage of carbon in biomass as determined by ultimate analysis; H = percentage of hydrogen in biomass as determined by ultimate analysis; O = percentage of oxygen determined by difference on the dry and ash-free basis, i.e. O (db, ash-free) = 100 - C - H - N.

| Sample               | Calorimeter (MJ/Kg) | Calculation (Sheng and Azevedo) |
|----------------------|---------------------|----------------------------------|
| Control Shell        | 16.82               | 14.27                            |
| Torrefaction Shell   | 20.27               | 19.11                            |

Based on the results of the measurements and calculations using the ultimate data, it was shown that the palm shell torrefaction had a higher HHV value than the palm shell without torrefaction. This can occur because of an increase in the amount of carbon content in palm kernel shells that have undergone torrefaction and the elimination of some chemical compounds in palm kernel shells that have the potential to cause smoke, especially mild volatile during the process of torrefaction such as water, acetic acid, and phenol[16]. During the torrefaction process, there is a thermal decomposition of hemicellulose, cellulose, and lignin into volatile substances causing decrease of O/C and H/C levels, thereby increasing the carbon content of palm kernel shells [12], [13], [24], [25]. Decomposed compounds have low energy including H_{2}O, CO, and CO_{2} and leave the polymer which has a higher C–C bond with energy. As a result, this is what causes an increase in the value of HHV palm kernel shells produced by torrefaction.

3.5. Weight loss, mass yield, energy yield, and energy density
There are several parameters that affect the quality of a biomass to be used as fuel, mainly related to its potential to be produced on a large scale, namely mass lost, mass yield, energy yield and energy density calculated using equation (1), (2), (3) and (4). The following result of calculating the efficiency parameters of the process.

| Parameter       | The calculation results |
|-----------------|-------------------------|
| Weight loss     | 35%                     |
| Mass yield      | 64.71%                  |
| Energy yield    | 0.78                    |
| Energy density  | 1.21                    |

The weight loss due to the torrefaction process was 35%, while the mass yield was 64.71%. Mass yield is a comparison between the mass before, and after torrefaction, an increase in torrefaction temperature caused decrease in mass yield, there are significant differences in the temperature range of 250-300 °C [13], [15]. The decrease in weight and mass yield was due to evaporation of water still
contained in the palm shell and the degradation of hemicellulose and some cellulose and lignin which produce volatile compounds such as organic acids and phenol [7], and some of the shells that burn into CO₂ due to conditions reactor that is not entirely inert.

Energy yield refers to the percentage of initial energy remaining after the torrefaction process [13]. From the calculation obtained an energy yield of 0.78. Generally, an increase in energy yield happens when the temperature of the reaction is increased to 250 °C. At this temperature, the loss mass is lower than 50% because at this temperature the process that occurs is mostly vaporization of water and hemicellulose degradation followed by an increase in caloric value. When the temperature is increased to 300 °C or more, it caused a decreased in energy yield due to a considerable decrease in mass of biomass because at this temperature thermal degradation has occurred not only in hemicellulose but also in lignin and cellulose [15], [25].

The decomposition of hemicellulose and cellulose leaves biochar with more carbon density [26]. Energy density is the energy stored in the biomass, this density also shows the length of flame time after combustion [25]. From the calculation, the value of the density of the palm kernel shells which extracted is 1.21, which means the amount of energy that can be stored in palm kernel shell is more than before torrefaction. The increase in energy density is because the composition of the palm kernel shell has a high lignin content, where biomass that is good for the torrefaction process has a high lignin content [26]. Energy density depends on energy yield while energy yield is dependent on HHV, with an increase in the temperature of torrefaction are associated with release of more aromatic compounds and increase in carbon content. This increases the degree of correlation and change of biomass structure into hydrophobic and brittle biochar [13], [15].

4. Conclusions
Torrefaction palm kernel shells using the COMB method at a temperature of 250 °C and 4 cm³/minute flowrate reduces moisture to a level of 5%, decreases volatile matter, increases bulk density, and increases ash content. Torrefaction also reduced O/C and H/C levels, which caused the HHV value of palm kernel shells from before and after torrefaction of 16.82 MJ/kg and 20.27 MJ/kg. The mass yield produced is 64.71%. Energy yield 0.78 with an energy density of 1.21. To sum up, palm kernel shells can be enhanced by their physicochemical characteristics through torrefaction with COMB method as a fuel.

5. Acknowledgments
The authors want to give thanks to Ministry of Research, Technology, and Higher Education of the Republic of Indonesia for supporting this research.

References
[1] Barta-Rajnaia E, Wangb L, Sebesténya Z, Bartad Z, Khalilb R, Skreibergb Ø, Grönlic M, Jakaba E and Czégénya Z 2017 Energy Procedia 105 551
[2] BPS 2019 “Badan Pusat Statistik,”[Online][Accessed: 05-Mar-2019]
[3] Thaim T and Rasid R A 2016 Aust. J. Basic Appl. Sci. 10 114
[4] Saelor S, Kongjan P and O-Thong S 2017 Energy Procedia 138 717
[5] Chen C, Qin S, Chen F, Lu Z and Cheng Z 2019 J. Energy Inst. 92 364
[6] Haryati S, Rahmatullah and Putri R W 2018 IOP Conf. Ser. Mater. Sci. Eng. 334
[7] Mafu L D, Neomagus H W J P, Everson R C, Carrier M, Strydom C A and Bunt J R 2016 Bioresour. Technol. 202 192
[8] Bach Q V, Skreiberg Ø and Lee C J 2017 Energi 138 348
[9] Zhang C, Wang C, Cao G, Chen W H and Ho S H 2019 Fuel 246 375
[10] Chen Z, Wang M, Ren Y, Jiang E, Jiang Y and Li W 2018 IOP Conf. Ser. Earth Environ. Sci. 113
[11] Hidayat W, Hasunudin U, Iryani D A, Amrul A, Lee S, and Kim S 2018 Annual International Symposium of Institute of Forest Science (KNUIFS 2018) South Korea
[12] Faizal H M, Shamsuddin H S, Heiree M H M, Hanaffi M F M A, Rahman M R A, Rahman M M and Latiff Z A 2018 Renew. Energ. 122 419
[13] Pahla G, Mamvura T A, Ntuli F and Muzenda E 2017 South Afr. J. Chem. Eng. 24 168
[14] Sukarta I N and P. Sri Ayuni 2016 *J. Sains Dan Teknol.*, vol. 5, Aug. 2016.
[15] Mamvura T A, Pahla G, and Muzenda E 2018 *South Afr. J. Chem. Eng.* 25 1
[16] Suastika K G, Karelius K, Dirgantara M, and Rumbang N 2019 *Risal. Fis.* 3 47
[17] Yemura Y, Sellappah V, Trinh T H, Komiyama M, Hassan S and Tanoue K 2018 *IOP Conf. Ser. Mater. Sci. Eng.* 458
[18] Samad N A F A, Jamin N A, and Saleh S 2017 *Energy Procedia* 138 313
[19] Chen Y C, Chen W H, Lin B J, Chang J S and Ong H C 2017 *Energy Procedia* 105 108
[20] Susanty W, Helwani Z and Zulfansyah 2016 *J. Online Mhs. Fak. Tek. Univ. Riau* 3 1
[21] Wang L, Barta-Rajnai E, Skreiberg Ø, Khalil R, Czégény Z, Jakab E and Grønli M 2017 *Energy Procedia* 105 1149
[22] Jagodzińska K, Gądek W, Pronobis M and Kalisz S 2019 *IOP Conf. Ser. Earth Environ. Sci.* 214
[23] Elneel R, Anwar S and Ariwahjoedi B 2013 *J. Appl. Sci.* 13 491
[24] Tumuluru J S, Sokhansanj S, Wright C T, Hess J R and Boardman R D 2011 *Symp. Thermochem. Convers.* 1
[25] Alamsyah R, Siregar N C and Hasanah F 2017 *IOP Conf. Ser. Earth Environ. Sci.* 65
[26] Pahla G, Ntuli F and Muzenda E 2018 *Waste Manag.*, vol. 71 512