JPSE (Journal of Physical Science and Engineering), Vol. 8, No. 2, 2023, Page 119–129.
DOI: 10.17977/um024v8i22023p119

JPSE
(Journal of Physical Science and Engineering)

http://journal2.um.ac.id/index.php/jpse
EISSN: 2541-2485

Significance of Torrefaction Effect on Energy Properties Palm Kernel Shell

Received
1 April 2023

Revised
21 September 2023

Accepted for Publication
29 October 2023

Published
30 October 2023

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Abstract

The process of torrefaction is a thermochemical process that is widely used for the conversion of biomass into renewable fuels. In this study, the significance of temperature was determined by carrying out the torrefaction process at temperatures ranging from 275 to 350 degrees Celsius with a fixed residence time of 60 minutes. To ascertain the impact of time on the process, the torrefaction procedure was conducted over a residence time of 20 to 60 minutes at 300°C. Increasing the torrefaction temperature can substantially increase the palm kernel shell's calorific value, decrease water content, decrease volatility, increase fixed carbon, especially from 275 °C to 325 °C, and decrease ash content from 275 °C to 300 °C. Increasing the torrefaction residence time can significantly increase the palm kernel shell's calorific value from 20-40 minutes, decrease ash content and volatile content, and increase fixed carbon from 20-30 minutes. The residence time did not affect the water content in torrefaction temperature at 300 °C. The statistical analysis revealed that temperature and residence time have a substantial impact on the heating value and proximate analysis.

Keywords: Calorific Value, Proximate, Residence Time, Temperature, Torrefaction

1. Introduction

Biomass is renewable energy with neutral CO_2, which does not affect the CO_2 concentration in the atmosphere[1], [2]. Compared to fossil fuels, biomass has low sulfur and nitrogen content, so it does not cause pollutants such as SO_2 and NO_x released after combustion [3]. Biomass consists of organic materials that can be used as energy sources, both heat and electricity, through transformation processes, both thermal and chemical [4], [5]. This organic material is straightforward to find, environmentally friendly, and has economic value. It is a by-product of primary products, including plantations, agriculture, forestry, and urban waste [2], [6], [7]. Based on the existing criteria, biomass is one of the attractive raw materials for power generation and a substitute for coal.

Torrefaction is a thermochemical process that aims to improve biomass quality as fuel by increasing the calorific value and carbon content [8], [9], [10]. Torrefaction with the batch method is generally carried out in a temperature range of 200-350 ^{0}C with a temperature holding time of 30-60 minutes under inert conditions and ambient atmospheric pressure [11], [12], [13], [14]. Torrefaction is also often called a light pyrolysis process that thermochemically changes biomass structure by removing moisture and light volatiles [13]. The difference between torrefaction and pyrolysis is the temperature used [15], [16], [17]. The pyrolysis process uses a higher temperature, resulting in the total evaporation of volatile compounds. The torrefaction process has by-products that can be grouped into two groups based on whether or not it can be condensed. The by-products are water, carbon dioxide (CO_2), carbon monoxide (CO), and various organic compounds resulting from the condensation of biomass steam [18].

Calorific and proximate analysis is an essential parameter in fuel which is a reference for fuel quality in various standards in the world[19], [20], [21]. Previous studies have not employed statistical methods to investigate the actual differences in energy parameters such as calorific value, moisture content, ash content, fixed carbon, and volatile matter resulting from variations in temperature and residence time. This paper will examine the impact of elevated temperature and extended residence time on the torrefaction process on palm kernel shell biomass's calorific value and proximate composition. The effect of temperature and residence time on calorific and proximate values was determined using Analysis of Variance (ANOVA) at the 5% significance level, followed by the Duncan Multiple Range Test (DMRT).

2. Method

2.1 Raw material preparation and torrefaction

The raw material palm kernel shells are obtained from palm oil production. The biomass is then dried to reduce the water content of the shell to below 5%. Drying is done by heating an oven at 105 °C for 15 minutes [22], [23], [24].

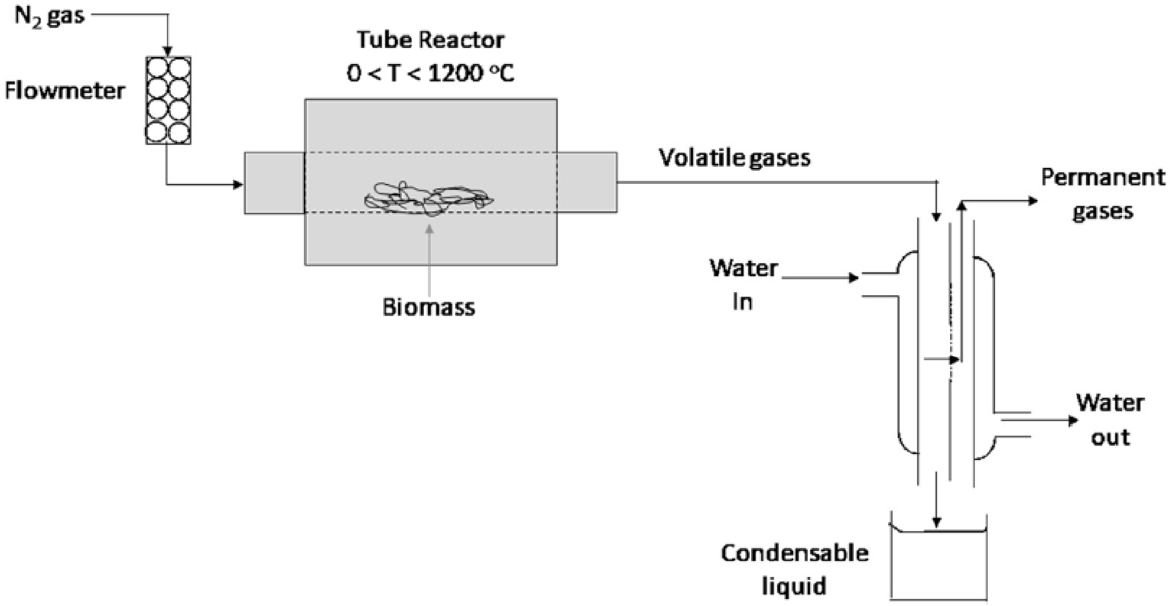

Figure 1. Torrefaction Process [18]

The torrefaction process is shown in Figure 1 [18], with the biomass container modified into a shelf to increase heat absorption in the biomass [25]. In Figure 1, nitrogen gas is distributed at 2 liters/minute for 10 minutes until the torrefaction reactor conditions are inert. The torrefaction process was carried out at 275 °C, 300 °C, 325 °C, and 350 °C with holding times of 20, 30, 40, 50, and 60 minutes.

2.2 Proximate and calorific analysis

This study tested proximity analysis to determine moisture, volatile, and ash content with ASTM D3171, D3175, and D3174 standards [26], [27]. Analysis of calorific values aims to determine the Higher Heating Value (HHV) and Lowest Heating Value (LHV) are carried out by following the ASTM D240 procedure using bomb calorimetry [26].

2.3 Statistical Analysis

The data obtained were analyzed using R 4.0.3 for Windows. The data from the measurement of heat were processed using the Analysis of Variance (ANOVA) test to ascertain whether there was a difference in the mean value of all treatment groups. If the results of the ANOVA test indicated a significant difference at the level of significance, then the Duncan Multiple Range Test (DMRT) was employed to identify the differences between each treatment group. The following hypotheses were employed in this study:

ANOVA test for the effect of temperature on calorific value is done with the following hypotheses:

H_0: *all temperatures give the same calorific value*
H_1: *there are at least a pair of temperatures that share different heating values*

The ANOVA test for the effect of temperature on water content is done with the following hypothesis:
H_0: *all temperatures give the same water content*
H_1: *there are at least a pair of temperatures that give different water content*

The ANOVA test for the effect of temperature on ash content is done with the following hypothesis:
H_0: *all temperatures give the same ash content*
H_1: *there are at least a pair of temperatures that give different ash content*

The ANOVA test for the effect of temperature was carried out with the following hypothesis:
H_0: *all temperatures give the same volatile*
H_1: *there are at least a pair of temperatures that give different volatile*

The ANOVA test for the effect of temperature on fixed carbon is done with the following hypothesis:
H_0: *all temperatures give the same fixed carbon value*
H_1: *there are at least a pair of temperatures that share different fixed carbon values*

ANOVA test for the impact of residence time on the calorific value is done with the following hypotheses:
H_0: *all times give the same calorific value*
H_1: *there are at least a pair of times that share different calorific values*

ANOVA test for the effect of time on water content is done with the following hypothesis:
H_0: all times give the same water content
H_1: there are at least a *pair of times that show the different moisture content*

ANOVA test for the effect of time on ash content is done with the following hypotheses:
H_0: *all times give the same ash content*
H_1: *there are at least a pair of times that give different ash content*

ANOVA test for the effect of time on volatile is done with the following hypothesis:
H_0: *all times give the same volatile*
H_1: *there are at least a pair of times that give different volatile*

ANOVA test for the effect of time on fixed carbon is done with the following hypothesis:
H_0: *all times give the same fixed carbon value*
H_1: *there are at least a pair of times that share different fixed carbon values*

3. Results and Discussion

3.1 Torrefaction effect on visual

The first step to determine if the torrefaction process is going well is visual, where after torrefaction, the biomass will turn black like charcoal. Visually, the black color of the torrefaction palm shell looks evenly distributed, and there is no brown part of the shell, as shown in Figure 2. This indicates that the torrefaction process has been going well. The difference in the effect of temperature and residence time is not visible visually; therefore, further tests are needed to find out.


Control After Torrefaction

Figure 2. Palm Kernel Shell Before and After Torrefaction Process

3.2 Temperature effect on calorific value and proximate analysis

The torrefaction process was carried out to determine the impact of temperature between 271-350°C with a residence time of 60 minutes.

3.2.1 Temperature effect on calorific value

Based on the results of the ANOVA test in Table 1, the p-value of 0.000 is smaller than the significance level of =5%, so it can be concluded that there are at least a pair of temperature treatments that provide different calorific values at a residence time of 60 minutes. Furthermore, to see the temperature treatment pairs that provide additional heat, the DMRT Advanced test is carried out to see the temperature pairs that provide different heat responses. The test results are presented in Table 2. Other letter notations in one column conclude that the two treatments differ in heat at a 5% significance level.

Table 1. ANOVA Result for Temperature and calorific

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Temperature	3	1549735	516578	44.54	0.000
Residual	8	92793	11599		

Table 2. DMRT Results for temperature and calorific

Treatment	Average of Calorific Value (Cal/g)
275 °C	5759.80 ^{a}
300 °C	6322.28 ^{b}
325 °C	6563.98 ^{c}
350 °C	6699.89 ^{c}

The letters a, b, c in the table indicate whether or not there is a significant difference between the treatments.

When palm kernel shells are heated in a special way called torrefaction, they become more energy-rich. This is because the amount of carbon in the shells increases, and some chemicals that can cause smoke are removed [10], [28]. This makes the shells burn more efficiently. During torefaction, hemicellulose breaks down into smelly substances and the levels of oxygen, and hydrogen decrease [29]. This makes more carbon get stuck in the palm kernel shell . Based on the results of Duncan's test, the calorific value of 275 °C has a significant difference from the calorific value of 300 °C, the calorific value of 325 °C, and the calorific value of 350 °C. The calorific value at 300 °C was significantly different from 325 °C and 350 °C. The calorific value at 325 °C and 350 °C has no difference. Finally, we can conclude that increasing the torrefaction temperature can significantly increase the palm kernel shell's calorific value, especially from 275 °C to 325 °C.

3.2.2 Temperature effect on water content

Based on the results of the ANOVA test in Table 3, the p-value of 0.02 is smaller than the significance level of 5%. So, it can be concluded that there is a significant temperature difference. Then, at least a pair of temperatures give significantly different water content. Furthermore, to see the temperature treatment pairs that provide additional water content, the DMRT Advanced test is carried out. The test results are presented in Table 4. Different letter notations in one column conclude that the two treatments provide a difference in heat at a 5% significance level.

Table 3. ANOVA Result for Temperature and Water Content

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Temperature	3	2.6616	0.8872	12.34	0.002
Residual	4	0.5752	0.0719		

Table 4. DMRT Result for Temperature and Water Content

Treatment	Average of water content (%)
275 °C	2.87 ^{a}
300 °C	2.03 ^{b}
325 °C	1.89 ^{c}
350 °C	1.67 ^{c}

The letters a, b, c in the table indicate whether or not there is a significant difference between the treatments.

In general, the water content decreases as the temperature of the torefaction process increases. The amount of water in a substance can affect how well it burns. When there's too much water, the grinding machine parts will wear down. Another thing that is influenced by the amount of water is how much energy is released when something burns. More water in the solid fuel means more heat is needed to burn it, which uses up more energy [30], [31]. Also, if there is a lot of water in the material and it is kept in a closed container for a long time, it can become a fire hazard. This is because the high humidity can cause fermentation, which can make the material hot and potentially start a fire if there is friction or if the material is near a heat source. Based on the results of Duncan's test, the water content of 275 °C has significant differences in water content at temperatures of 300 °C, 325 °C, and 350 °C. The water content at a temperature of 300 °C was significantly different from 275 °C. The water content of 300°C was not substantially other from the water at 325 °C and 350 °C. The water content at a temperature of 325 °C and 350 °C had no significant difference. Finally, we can conclude that increasing the torrefaction temperature can significantly decrease the palm kernel shell's water content, especially from 275 °C to 325 °C.

3.2.3 Temperature effect on ash content

Based on the test results in Table 5, the p-value of 0.0006 is smaller than the significance level = 5%. So, it can be concluded that there is a significant difference in the effect of temperature on the ash content. Then, at least a pair of temperatures give significantly different ash content. Furthermore, to see the temperature treatment pairs that gave additional ash content, the DMRT continued test was carried out. The test results are presented in Table 6. Other letter notations in one column conclude that the two treatments differ in ash content at a 5% significance level.

Table 5. ANOVA Result for Temperature and Ash Content

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Temperature	3	9.672	3.224	8.23	0.0006
Residual	8	1.415	0.177		

Table 6. DMRT Result for Temperature and Ash Content

Treatment	Average of ash content (%)
275 °C	4.98^{a}
300 °C	3.18^{bc}
325 °C	2.90^{c}
350 °C	2.74^{c}

The letters a, b, c in the table indicate whether or not there is a significant difference between the treatments.

Ash is the leftover organic material after burning solid fuel. The more ash in a fuel, the less heat it gives off. A small amount of ash is also really important when turning plants into energy, especially if the plants have potassium or chlorine in them. These chemicals can damage equipment used to turn plant and animal waste into gas. Through torefaction, minerals are lost, causing the biomass to have less ash. This happens because water, carbon dioxide, and carbonates turn into vapor. Also, other chemical compounds change into oxides through oxidation[18], [32]. Based on the results of Duncan's test, the ash content at a temperature of 275 °C has a significant difference from the ash content at a temperature of 300 °C, 325 °C, and 350 °C. The ash content at the temperature of 300 °C did not significantly differ from the ash content at 325 °C and 350 °C. Ash content at a temperature of 325 °C and 350 °C also did not vary substantially. Finally, we can conclude that increasing the torrefaction temperature can considerably decrease the palm kernel shell's ash content, especially from 275 °C to 300 °C.

3.2.4 Temperature effect on volatile

Based on the test results in Table 7, the p-value of 0.0001 is smaller than the significance level of 5%. So, it can be concluded that there is a significant difference in the effect of temperature on volatile. Then there is at least a pair of temperatures that give different fluctuations. Furthermore, to see the temperature treatment pairs that provide additional volatile, the DMRT Advanced test is carried out to see the temperature pairs that respond to the magnitude of different volatile values. The test results are presented in Table 8. Other letter notations in one column conclude that the two treatments provide significant differences in volatility at a 5% significance level.

Table 7. ANOVA Result for Temperature and Volatile

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Temperature	3	378.4	126.14	26.33	0.0001
Residual	8	38.3	4.79		

Table 8. DMRT Result for Temperature and Volatile

Treatment	Average of volatile (%)
275 ^{o}C	44.68 ^{a}
300 ^{o}C	33.91 ^{b}
325 ^{o}C	32.58 ^{c}
350 ^{o}C	29.94 ^{c}

The letters a, b, c in the table indicate whether or not there is a significant difference between the treatments.

As the temperature goes up, the amount of smelly compounds goes down. Volatile compounds are made up of gases that can easily catch fire, like hydrogen, carbon monoxide, and methane, and a small amount of vapors that can turn into liquid, like tar, and other substances that form when things get very hot, like carbon dioxide and water [28], [33]. Based on the results of Duncan's test, the volatile at 275 ^{o}C has a significant difference from the volatile at 300 ^{o}C, 325 ^{o}C, and 350 ^{o}C. The volatile value at the temperature of 300 ^{o}C has a substantial difference from the volatile at 325 ^{o}C and 350 ^{o}C. Volatile values at 325 ^{o}C and 350 ^{o}C did not significantly differ. Finally, we can conclude that increasing the torrefaction temperature can substantially decrease the palm kernel shell's volatility, especially from 275 ^{o}C to 325 ^{o}C.

3.2.5 Temperature effect on fixed carbon

This measure of carbon content indicates the remaining organic material in the fuel after it has decomposed, as well as other elements such as nitrogen, sulfur, hydrogen, and possibly oxygen.The amount of carbon that doesn't change is connected to how easily the material burns. A biomass with less volatile content will have a higher concentration of solid carbon, leading to more efficient burning [34], [35]. Based on the test results in Table 9, the p-value of 0.0001 is smaller than the significance level of 5%. So it can be concluded that there is a significant difference in the effect of temperature on the fixed carbon value. Then, at least a pair of temperatures give different fixed carbon. Furthermore, to see the temperature treatment pairs that provide additional fixed carbon, the DMRT Follow-up test is carried out to see the temperature pairs that respond to the magnitude of the other fixed carbon values. The test results are presented in Table 10.

Different letter notations in one column conclude that the two treatments differ on fixed carbon at a significant level of 5%.

Table 9. ANOVA Result for Temperature and Fixed Carbon

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Temperature	3	584.4	194.80	28.57	0.0001
Residual	8	54.6	6.82		

Table 10. DMRT Result for Temperature and Fixed Carbon

Treatment	Average of fixed carbon
275 ^{o}C	47.45 ^{a}
300 ^{o}C	60.88 ^{b}
325 ^{o}C	62.63 ^{c}
350 ^{o}C	65.69 ^{c}

The letters a, b, c in the table indicate whether or not there is a significant difference between the treatments.

Based on Duncan's test results, the value of fixed carbon at 275 °C has a significant difference from fixed carbon at a temperature of 300 °C, 325 °C, and 350 °C. The fixed carbon value at 300 °C significantly differs from the fixed carbon value at 325 °C and 350 °C. However, fixed carbon at a temperature of 325 °C and 350 °C did not vary substantially. Finally, we can conclude that increasing the torrefaction temperature can significantly decrease the palm kernel shell's fixed carbon, especially from 275 °C to 325 °C.

3.3 Residence time effect on calorific value and proximate analysis

The torrefaction process to determine the impact of residence time between 20-60 minutes is carried out at a temperature of 300 ºC

3.3.1 Residence time effect on calorific value

Based on the test results in Table 11, the p-value of 0.001 is smaller than the significance level of 5%. So it can be concluded that at least a pair of time treatments provide different calorific values at a torrefaction temperature of 300 C. Furthermore, to see the temperature treatment pairs that provide different calorific values, the DMRT further test is carried out. The test results are presented in Table 12. Other letter notations in one column conclude that the two treatments provide a difference in heat at a 5% significance level.

Table 11. ANOVA Result for Residence Time and Calorific Value

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Time	4	335683	83921	9.441	0.001
Residual	10	88889	8889		

Table 12. DMRT Result for Residence Time and Calorific Value

Treatment	Average of Calorific Value (Cal/g)
20 minutes	5911.64^{a}
30 minutes	6101.57^{b}
40 minutes	6176.95^{bc}
50 minutes	6302.18^{cd}
60 minutes	$6322.28a^{ce}$

The letters a, b, c, d, e in the table indicate whether or not there is a significant difference between the treatments.

The calorific value of a substance increases with the duration of its residence within the terefaction process. Based on the results of Duncan's test, the calorific value at 20 minutes has a significant difference frodm the calorific value at 30, 40, 50, and 60 minutes. The calorific value at residences of 30 minutes and 40 minutes did not significantly differ, while 30 minutes had a significant difference with 50 and 60 minutes residences. The residence time of 40 minutes, 50 minutes, and 60 minutes did not significantly differ from the amount of heat. Finally, we can conclude that increasing the torrefaction residence time can substantially increase the palm kernel shell's calorific value, especially from 20-40 minutes.

3.3.2 Residence time effect on water content

Table 13. ANOVA Result for Residence Time and Calorific Value

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Time	4	0.0001390	3.474×10^{5}	2.934	0.0763
Residual	10	0.0001184	1.184×10^{5}		

Based on the test results, the p-value of 0.0764 is higher than the significance level of =5%. So it can be concluded that there is no significant difference in water content. At this stage, the DMRT test was unnecessary because the residence time did not affect the water content at the torrefaction temperature of 300 °C. The average water content of torrefaction with a temperature of 300 °C is 2.45%.

3.3.3 Residence time effect on ash content

Based on the test results in Table 14, the p-value of 0.000 is smaller than the significance level of 5%. So it can be concluded that there is a significant difference in the effect of time on the ash content. So there is at least a pair of times that give significantly different ash content. Furthermore, to see the time treatment pairs that gave additional ash content, the DMRT continued test was carried out to see the time pairs that gave different ash content responses. The test results are presented in Table 15. Other letter notations in one column conclude that the two treatments differ in ash content at a 5% significance level.

Table 14. ANOVA Result for Residence Time and Ash Content

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Time	4	0.00113	2.829×10^{-4}	21.89	0.000
Residual	10	0.00012	1.292×10^{-5}		

Table 15. DMRT Result for Residence Time and Ash Content

Treatment	Average of Ash Content (%)
20 minutes	0.052^{a}
30 minutes	0.032^{b}
40 minutes	0.029^{b}
50 minutes	0.030^{b}
60 minutes	0.032^{b}

The letters a, b, in the table indicate whether or not there is a significant difference between the treatments.

Based on the results of Duncan's test, the ash content at 20 minutes had a significant difference from the ash content produced at 30 minutes, 40 minutes, 50 minutes, and 60 minutes at the same temperature, which is 300 °C. While the ash content at temperatures of 30 minutes, 40 minutes, 50 minutes, and 60 minutes did not produce a significant difference. Finally, we can conclude that increasing the torrefaction residence time can significantly decrease the palm kernel shell's ash content, especially from 20-30 minutes.

3.3.4 Residence time effect on volatile

Based on the results of the ANOVA test in Table 16, the p-value of 0.00025 is smaller than the significance level of 5%. So it can be concluded that there is a significant difference in the effect of time on volatility. So there are at least a pair of times that provide different volatility. Furthermore, to see the treatment pairs that provide additional volatile, the DMRT Follow-up test is carried out to see the time pairs that respond to the magnitude of the different volatile values. The test results are presented in Table 17. Other letter notations in one column conclude that the two treatments provide significant differences in volatility at a 5% significance level.

Table 16. ANOVA Result for Residence Time and Volatile

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Time	4	0.0244	0.006	15.84	0.00025
Residual	10	0.0038	0.0003		

Table 17. DMRT Result for Residence Time and Volatile

Treatment	Average of Volatile (%)
20 minutes	0.45^{a}
30 minutes	0.37^{b}
40 minutes	0.35^{b}
50 minutes	0.34^{b}
60 minutes	0.34^{b}

The letters a, b, in the table indicate whether or not there is a significant difference between the treatments.

Based on Duncan's test results, the volatile at 20 minutes significantly differs from the volatile generated at 30 minutes, 40 minutes, 50 minutes, and 60 minutes, at the same temperature, 300 °C. Meanwhile, the volatile at 30 minutes, 40 minutes, 50 minutes, and 60 minutes did not produce a significant difference. Finally, we can conclude that increasing the torrefaction residence time can significantly decrease the palm kernel shell's volatility, especially from 20-30 minutes.

3.3.5 Residence time effect on fixed carbon

Based on the test results in Table 18, the p-value of 0.00016 is smaller than the significance level of 5%. So it can be concluded that there is a significant difference in time on the fixed carbon value. So there is at least a pair of times that give different fixed carbons. Furthermore, to see the time treatment pairs that provide additional fixed carbon, the DMRT Advanced test is carried out to see the time pairs that respond to the magnitude of the different fixed carbon values. The test results are presented in Table 17. Other letter notations in one column conclude that the two treatments differ on fixed carbon at a significant level of 5%.

Table 18. ANOVA Result for Residence Time and Fixed Carbon

Source of diversity	Degrees of Freedom	Sum of total squares	Least Square Method	F count	p-value
Time	4	0.037	0.0093	17.49	0.00016
Residual	10	0.005	0.00053		

Table 19. DMRT Result for Residence Time and Fixed Carbon

Treatment	Average of Fixed Carbon (%)
20 minutes	0.47^{a}
30 minutes	0.58^{b}
40 minutes	0.60^{b}
50 minutes	0.60^{b}
60 minutes	0.61^{b}

The letters a, b, in the table indicate whether or not there is a significant difference between the treatments.

Based on Duncan's test results, fixed carbon at 20 minutes had a significant difference, with fixed carbon produced at 30 minutes, 40 minutes, 60 minutes, and 60 minutes at the same temperature, 300 °C. In comparison, fixed carbon at temperatures of 30 minutes, 40 minutes, 50 minutes, and 60 minutes did not produce a significant difference. Finally, we can conclude that increasing the torrefaction residence time can significantly increase the palm kernel shell's fixed carbon, especially from 20-30 minutes.

4. Conclusion

Temperature and residence time significantly affect the heating value and proximate based on the statistical analysis. Increasing the torrefaction temperature can substantially increase the palm kernel shell's calorific value, decrease water content, decrease volatility, increase fixed carbon, especially from 275 °C to 325 °C, and decrease ash content from 275 °C to 300 °C. Increasing the torrefaction residence time can significantly increase the palm kernel shell's calorific value from 20-40 minutes, decrease ash content and volatile content, and increase fixed carbon from 20-30 minutes. The residence time did not affect the water content in torrefaction temperature at 300 °C.

Acknowledgment

This work was supported by Badan Pengelola Dana Perkebunan Kelapa Sawit (BPDPKS) who have funded through the Grant Palm Research Scheme.

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