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Valorization of corncob through torrefaction process

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Abstract. Corncobs is a waste of post-harvest corn processing that has great potential to be used as a source of renewable solid fuel. Its high moisture and volatile solids content produces a lot of smoke when corncob is burned, so it is rarely used as fuel. This study aims to improve the quality of corncob fuel through the torrefaction process. The corncob was naturally dried using sunrays for two days and cut into pieces of 1-3 cm in size. The torrefaction process was carried out using a cylindrical rotary reactor which operated at a speed of 30 RPM and was heated using an external heat source. The variations of torrefaction time were 30, 40, and 60 minutes. The parameters to be observed included moisture content, ash content, volatile content, calorific value, and hydrophobicity of materials. The results showed that the torrefaction process improved the quality of corncobs as seen from an increase in calorific value, an increase in hydrophobicity. In this study, the calorific value of the torrefied corncobs was 18.89 MJ/kg to 21.61 MJ/kg, which was higher than the calorific value of the non-torrefied corncobs of 17.66 MJ/kg. The torrefied corncobs are also more hydrophobic and absorb less water than the non-torrefied corncobs.

1. Introduction

Corn is a food crop that is cultivated on dry land. In Lampung Province, corn is the farmer's choice after cassava. In 2017, the planting area for corn reached 482,607 ha with a production of 2,518,894 ton and a productivity of 52.19 ton/ha [1]. In 2019, maize production in Lampung Province slightly decreased to 2,374,384 ton [2]. Corn and cassava are planted on the same land so that the area of the corn will catch up with cassava and is largely determined by the prices of these two commodities. When the price of cassava is high, farmers will flock to plant cassava, causing an oversupply and decreasing the price of cassava. On the other side, when the price of corn is good, farmers plant corn so that corn production is excessive and the price falls.

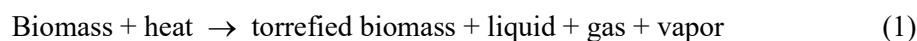
Corn is harvested at the age of 100-120 days depending on needs. Harvesting and post-harvest activities (especially shelling) of maize produce waste biomass in the form of stalks, leaves, and corn husks left on the field, as well as corncobs and chaff (*jenjet*) produced during corn shelling. The composition of maize waste biomass per unit plant area (ha) is presented in Table 1. Overall, the amount of corn waste biomass reaches around 3 ton/ha with a composition of about 1 ton/ha corn cobs and 2 tons/ha corn stalks [3].

Table 1. Composition of corn waste biomass [3]

Location	Type of waste	Quantity (kg (%))	Energy value (MJ/kg)
Field	Stalks	864 (28.5)	15.66
	Leaf	672 (22.2)	15.20
	Husk	472 (15.6)	15.56
Corn shelling	Cobs	1.008 (33.3)	17.66
	Chaff	10 (0.3)	17.22
TOTAL		3.026 (100)	

Currently, most of the waste biomass from maize (stalks and cobs) is still being disposed of or managed in a bad manner. The amount of corncobs waste ranges from 20 to 25% of corn and is influenced by harvesting time. Corn harvested at the age of 100 days is still not so dry that it produces up to 25% corncobs waste. Meanwhile, corn harvested at the age of 120 days is dry enough and produces 20% corncobs. Corncobs can be used as fuel to substitute wood. Utilization of corn waste as an energy source faces obstacles like other biomass wastes in general, where untreated biomass has a high moisture content and low density so that energy density becomes low [4,5]. The low bulk density also complicates logistics and transportation. Biomass is also hygroscopic, thus reducing storage capacity. High levels of volatile materials result in low combustion efficiency and produce a lot of smoke. In addition, the high content of inorganic materials (Ca, Si, K) causes ash-related problems (sintering, fusion, agglomeration, slagging) [6,7].

The quality of corncobs fuel can be improved through the torrefaction process. Torrefaction is a thermal process that can overcome most of the issues related to the weakness of biomass as a fuel. Torrefaction involves heating biomass to a temperature of 200 - 300 °C in a state without or with limited oxygen [5] and a low heating rate or long enough residence time (30 minutes - 2 hours). Torrefaction is similar to pyrolysis at low temperatures and heating rates. Torrefaction produces brown-black material, a solid fuel similar to coal which has better fuel characteristics than the original biomass [8]. The torrefaction method is a promising technique for improving the quality of solid biomass [9]. The process of torrefaction destroys the bonds inherent in the biomass. Hemicellulose will be decomposed first and followed by cellulose and lignin decomposition, respectively [10]. We have reported that torrefaction is able to improve fuel quality of biomass pellet made of oil palm empty fruit bunch [11–15]. The structure of the biomass changes in such a way that the material becomes brittle, and more hydrophobic. In general, the pyrolysis reaction can be presented as follows:



The products of torrefaction consist of 80% solid (including charcoal and ash), 15% liquid (water, organic, fat), and 5% gas (CO₂, CO, CH₄, H₂, C_xH_y) [16,17]. The solid product in the form of torrefied biomass is the desired product from the torrefaction process [18]. The torrefied biomass is similar to coal [19] and has the following properties:

- Hydrophobic (does not like water) due to the destruction of the O – H bond structure so that it is unable to retain or absorb water. This is very advantageous for the process of handling, storage and transportation. The biological activity (decomposition, fungus, decay) of the biomass is also very low, thus extending the shelf life without degradation.
- The torrefaction biomass is more brittle, thus reducing the energy for grinding up to 80-90% compared to the original biomass. The particle size and distribution of the milled biomass torrefaction is more uniform than that of the original biomass. The torrefaction biomass has a degree of grind (grind ability) comparable to that of coal. Facilitates the biomass pelletization process because the lignin fraction increases 10-15% and the higher the fat structure increases the binding power. Biomass pellets that have a torrefaction are 1.5 to 2 times stronger, so they do not break easily in the handling and storage process.

- c. The porosity of the torrefaction product increases so that the fuel becomes more reactive during combustion and gasification. The torrefaction biomass has an O/C ratio and a low volatile substance content thereby improving combustion quality (smokeless) and resulting in high efficiency during gasification. The torrefaction biomass has a reactivity comparable to that of wood. Energy density also increases because the mass of biomass decreases to about 70% while the energy value decreases to 90% from the initial value so that the energy per unit mass increases to about 1.3 times the initial value.
- d. Torrefaction produces a homogeneous output (physical and chemical properties) of the mixed biomass, allowing pelletization of various types of biomass with one machine only and increasing the economy of biomass pellets. This allows the use of multiple types of wood biomass for energy with a single combustion device thereby increasing fuel availability, supply reliability, and lowering fuel costs and reducing handling and storage costs.

The purpose of this study was to determine the effect of torrefaction on the quality of solid fuel from corncobs. In this study, the size of the corncob material and duration of torrefaction process were evaluated on the quality of fuel.

2. Materials and Methods

The research was conducted from August 2018 to November 2018 at the Laboratory of Agricultural Machinery Equipment and Power, Department of Agricultural Engineering, Faculty of Agriculture, University of Lampung.

2.1. Materials

Corncobs were obtained from PD Semangat Jaya in Bangunsari Village, Sub district of Negeri Katon, Pesawaran Regency, Lampung Province. Corncobs were sun-dried for 2 days till dry, then were cut into pieces of 1-3 cm in size.

2.2. Torrefaction process

The torrefaction process was carried out using a cylindrical rotary reactor with a diameter of 20 cm and a length of 50 cm which was heated from an external heat source (LPG stove). The reactor run at 18 RPM and a temperature range of 200–300 °C. The temperature was maintained by adjusting the stove flame and the distance between the stove and the reactor.

2.3. Treatment

This study uses two treatment factors. The first factor was the size of the corn cobs (S) with 3 levels of treatment, namely 1 cm (S1), 2 cm (S2) and 3 cm (S3). The second factor was the duration of torrefaction (T), with 3 levels of treatment, namely 30 minutes (T1), 45 minutes (T2) and 60 minutes (T3). Each treatment factor was repeated 3 times

2.4. Analysis and Measurement

The parameters in this study included bulk density, moisture content, ash content, volatile content, calorific value, and hydrophobicity of materials.

Bulk density (kg/L) was calculated from the mass (m , in kg) of corn cobs occupying a certain volume (v , in L). Bulk density was calculated using:

$$\text{Density} = \frac{m}{v} \quad (2)$$

Water content (MC) was measured gravimetrically using an oven (Memmert UM 500) at a temperature of 105 °C for 24 hours. Water content (in units of % wet weight) was calculated using:

$$MC = \frac{M_i - M_f}{M_i} \times 100\% \quad (3)$$

where M_i is the initial weight and M_f is the final weight of the sample.

Ash content and volatile content were measured by burning the oven-dry corn cobs (*DM*) using a furnace (Vulcan D-550) at 550 °C for two hours. Ash content and volatile content (VS) were calculated by weight of ash through Equations (4) and (5):

$$Ash = \frac{Ash}{DM} \times 100\% \quad (4)$$

$$VS = 100\% - Ash \quad (5)$$

The caloric value of ingredients was expressed in relative terms in units of MJ/kg and measured using a bomb calorimeter (Cal2k ECO). Meanwhile, the hydrophobicity of the material was measured by soaking the sample in water and calculating the mass of water absorbed by the material within a certain time.

5. Results and Discussion

3.1. Characteristics of corncobs

The physical and chemical characteristics of corncobs used in the study are described in Table 2. Corncobs have an average moisture content of 11.84%. This is a typical condition for agricultural products that are naturally dried in the sun. The ash content in corn cobs reached 2.20%. This value is not much different from the research results of Hastuti *et al.* [20], where corn cobs have an ash content of 2.01%. In this research, the value of the volatile solid content was obtained at 97.80% db or 86.22% wb.

Table 2. Physical and chemical characteristics of corn cobs

Characteristics	Unit	Value
Moisture content	% wb	11,84
Total solid (TS)	% wb	88,16
Ash content	% db	2,20
Volatile content (VS)	% db	97,80
Bulk density	kg/L	0,533
Energy value	MJ/kg	17,66
Hemicellulose	%	33.85
Cellulose	%	33.31
Lignin	%	26.03

Jamilatun and Supomo [21] reported that the value of volatile content in corn cobs was 85.57%. This shows that the results of this study (volatile content 88.16) are close to the results that have been published. In our study, the cellulose content was 33.85%, the hemicellulose content was 33.31%, and the lignin content was 26.03%. According to Winarsih [22], the content of cellulose, hemicellulose and lignin of corncob was 28.77, 31.58, and 28.97%, respectively. The difference can be due to the difference in the corncob material used. The composition is influenced by the variety, age and condition of the corncobs. In addition, it is also due to differences in the chemicals used to determine the content of cellulose, hemicellulose, and lignin. Winarsih's research used NaOH, while our study used H₂SO₄. The ash content of corncobs used in our study was 2.20%, close to the ash content of corncobs used in the study of Hastuti *et al.* [20] of 2.01%.

3.2. Effect of torrefaction on characteristics of corncobs

The characteristics of corncobs after torrefaction are presented in Table 3. In general torrefaction process has increased energy value and reduced water content of corncobs. Meanwhile, the change of ash content due to torrefaction is not consistent.

Table 3. Characteristics of corncobs after torrefaction

Characteristics	Unit	Value
Moisture content	%wb	2,52 – 3,21
Ash content	%db	0,68 – 2,60
Volatile content (VS)	%db	97,38 – 99,30
Energy value	MJ/kg	18,89 – 21,61

3.2.1. Moisture content

The water content of corncobs after torrefaction was in the range of 2.52 – 3.21%, which is considerably lower than before torrefaction (11.84%). Water content is one of the parameters in determining the quality of the biomass fuels which affects the heating value of combustion, the ease of ignition, combustion power and the amount of smoke produced [23]. High water content contributes to the low energy value and high smoke production. During torrefaction process, water content and volatile components evaporate resulting in dry material. As presented in Table 4, the effect of both factors (cut size and torrefaction duration) as well as their interaction on the final moisture content are not statistically significantly at $\alpha = 0.05$.

Table 4. Effect of corncobs cut size and torrefaction duration on water content (%wb).

Cut size	Torrefaction duration (min)			Average
	30	45	60	
1 cm	2.98	3.19	2.88	3.02 ^{NS}
2 cm	3.21	3.20	2.74	3.05 ^{NS}
3 cm	2.57	2.52	2.55	2.55 ^{NS}
Average	2.92 ^{NS}	2.97 ^{NS}	2.72 ^{NS}	

Note: NS = not statistically different based on DMRT (Duncan's multiple range test) with level of significance $\alpha = 0.05$.

3.2.2. Ash and volatile content

Table 5 shows ash content of torrefied corncobs. In general, the effect of torrefaction on ash content of corncobs is fluctuating. Increasing torrefaction duration has a tendency to result in the increase of ash content from 0.94% at 30 min to 1.76% at 60 min. The effect of torrefaction duration on the ash content, however, was not statistically different by DMRT at significance level of $\alpha = 0.05$. The cut size of corncobs has a significant effect on the ash content of corncobs at $\alpha = 0.05$. The table reveals that increasing cut size has resulted in the decline of ash content from 2.17% with cut size of 1 cm to 0.83% with cut size of 3 cm. The Duncan's test showed that ash content of torrefied corncobs with a size of 1 cm was significantly higher than that of sizes 3 cm. There was no difference in ash content between torrefied corncobs with a size of 1 cm and that of 2 cm as well as ash content with a size of 2 cm and that of 3 cm.

Table 5. Effect of cut size and torrefaction duration on the ash content (%TS) of corncobs.

Cut size	Torrefaction duration (min)			Average
	30	45	60	
1 cm	1.75	2.17	2.6	2.17 ^a
2 cm	0.4	1.59	1.63	1.21 ^{ab}
3 cm	0.68	0.74	1.06	0.83 ^b
Average	0.94 ^{NS}	1.50 ^{NS}	1.76 ^{NS}	

Note: Values followed by same letter in column is not statistically different at DMRT with level of significance $\alpha = 0.05$. NS = not statistically different.

Volatile solid (VS) content directly relates to ash content and is calculated based on equation (5). The effect of torrefaction duration and cut size on VS content is therefore similar to their effect on ash content. The results of the average volatile content of the torrefied corncobs due to cut size was statistically different with a value as follows: 97.83% for 1 cm cut size, 98.79% for 2 cm cut size, and is 99.17% 3 cm cut size. Meanwhile, the average VS content due to torrefaction was not significantly different with a value of 98.89%, 98.49%, and 98.22%, respectively for torrefaction duration of 30, 45, and 60 minutes.

3.2.3. Hydrophobicity

In general, biomass is a hygroscopic material that easily absorbs moisture. Moisture in the biomass will trigger biological decomposition so that biomass quickly rotten. Another desirable advantage of the torrefaction process is to change the nature of the biomass from hydrophilic to be hydrophobic. Figure 1 shows the hydrophobicity characteristics of corncobs which is represented by the capability of corncobs to absorb water during immersion in water for 24 hours. Non-torrefied corncobs immediately absorb water and within 1 hour of soaking the water absorbed by corncobs reaches about 250%. In contrast, torrefied corncobs, have much lower water absorption, between 29.92% and 86.37% in the same immersion time. After 24 hours of soaking, raw corncobs were able to absorb water up to 350%, while torrefied corncobs ranged between 104.03% and 202.28%. This shows that the torrefaction process has increased the hydrophobicity of corncobs.

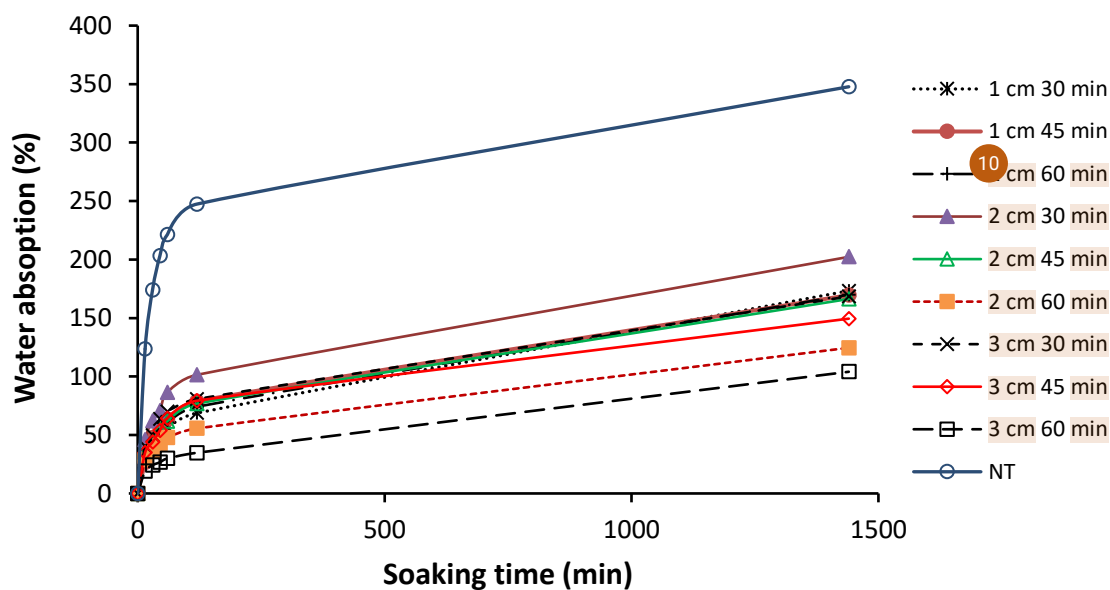


Figure 1. Water absorption capability of corncobs during soaking in water for 24 hours.

Table 5 shows the effect of treatment factors on the hydrophobicity of torrefied corncobs in term of their capability in absorbing or holding water after 24 hours soaking. It showed that the cut size had no significant effect on the hydrophobicity properties of torrefied corncobs. However, the duration of torrefaction had a significant effect on the hydrophobic properties of torrefied corncobs. Increasing torrefaction duration process tend to improve hydrophobicity of corncobs which is implied by lower water absorption capability. Duncan's test with $\alpha = 0.05$ shows that the hydrophobic nature of corncobs with a torrefaction duration of 30 minutes was significantly different from that of 60 minutes. The hydrophobic properties of corn cobs with a torrefaction of 45 minutes did not differ from the time of 60 minutes and 30 minutes.

Table 6. Effect of cut size and torrefaction duration on the hydrophobicity of corncobs (in % of absorbing water after 24 h soaking).

Cut size	Torrefaction duration (min)			Average
	30	45	60	
1 cm	173.23	169.54	169.97	170.92 ^{NS}
2 cm	202.28	166.29	124.53	164.37 ^{NS}
3 cm	168.47	149.44	104.03	140.65 ^{NS}
Average	181.33 ^a	161.75 ^{ab}	132.85 ^b	

Note: Values followed by same letter in row is not statistically different at DMRT. NS = not statistically different.

Hydrophobicity is a physical property of a molecular material that resists water absorption or repelling a water mass attraction. During torrefaction, hemicellulose decompose substantially and cellulose slightly. This result in higher proportion of lignin, a hydrophobic component, in the torrefied biomass. Hydroxyl group, which is responsible for binding and absorption of water, also decreases during torrefaction that resulting in a more hydrophobic material [24,25].

3.2.4. Energy value

After torrefaction, the corncobs change colour to brown to black and their weight will decrease. Table 7 shows the energy value of the raw corncobs as compared to that of torrefied corncobs based on their colour. This reveals that torrefaction process increases energy density of corncobs from 17.66 MJ/kg to the highest of 21.61 MJ/kg which is improvement of 22.4% as compared to the energy value of raw corncobs. During torrefaction process, hemicellulose is decomposed first and volatile substances are released, which in turn reduce O/C and H/C ratios. Reducing O/C and H/C ratios will increase energy density. This result is desirable because one of the purpose of torrefaction treatment is to increase heating value [26].

Table 7. Energy value of torrefied corncobs

Sample	Energy value (MJ/kg)
Dark brown	21.61
Light brown	18.89
Black	19.37
Yellow (raw)	17.66

4. Conclusion

Based on the above discussion, the following conclusions can be drawn:

1. The corncobs torrefaction process can improve the quality of corncobs in terms of water content, calorific value, hydrophobicity.
2. Torrefied corncobs had water content of 2.52 to 3.21% and the effect of cut size as well as torrefaction duration on the water content was not statistically significant at $\alpha = 0.05$.
3. Increasing cut size declined significantly on ash content of the torrefied corncobs from 2.17% with cut size 3 cm to 0.83% with cut size 1 cm.
4. The calorific value of torrefied corncobs was in the range of 18.89 MJ/kg to 21.61 MJ/kg, higher than that of raw or non torrefied corncobs of 17.66 MJ/kg.
5. Torrefied corncobs revealed a more hydrophobic nature with a capacity to absorb water of 104.03% to 202.28%, substantially lower than that of raw or non torrefied corncobs.

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