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# Investigation to Enhance Solid Fuel Quality in Torrefaction of Cow Manure

**Jiseok Hong, Changwon Chae, Hyunjoong Kim, Hyeokjun Kwon, Jisu Kim and Ijung Kim ***

Department of Civil and Environmental Engineering, Hongik University, Seoul 04066, Republic of Korea
* Correspondence: ijung.kim@hongik.ac.kr

**Abstract:** Recently, the conversion of livestock manure to solid fuel via torrefaction has brought more attention to moving forward to a carbon neutral society. A proper design of livestock manure to solid fuel is key for sustainable waste management. In this study, cow manure, as a representative of livestock manure, was examined for solid fuel production, focusing on enhancing the heating value. The torrefaction process was adopted as a main solid fuel generation process and compared to simple drying. The heating value of the torrefied cow manure was increased as the torrefaction temperature increased from 200 °C to 300 °C. The heating value was nearly saturated at around 30 min when the torrefaction temperature was increased from 20 min to 40 min. The heating value was further increased when the cow manure was mixed with sawdust or rice straw. The sawdust, which originally possessed a higher heating value, showed its potential as a candidate for additives to the torrefaction of cow manure. Compared to simple drying, torrefaction showed a higher heating value and energy density, successfully converting to stable carbon material.

**Keywords:** cow manure; sawdust; rice straw; torrefaction; drying; heating value

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## 1. Introduction

The livestock farming industry is experiencing rapid growth, alongside the global population [1,2], leading to a substantial increase in livestock waste worldwide. As of 2022 in Korea, major livestock species produced approximately 50.73 million tons of manure annually, with cattle accounting for more than 34% of the total [3]. The enormous volume of livestock manure not only generates unpleasant odors but also contributes to environmental issues such as soil and water contamination by heavy metals and antibiotics and the emission of greenhouse gases such as methane ($CH_4$) and nitrous oxide ($N_2O$) [4,5]. Therefore, there is an urgent need to investigate methods to mitigate the environmental problems associated with livestock manure.

In the era of the circular economy, a comprehensive strategy to convert livestock manure into renewable energy and/or resources is required, aiming for sustainable development goals for environmental protection. Composting and liquefaction are the principal technologies for converting livestock manure into valuable resources. However, the fertilization of livestock manure poses significant challenges, including the requirement for a large area as well as the potential release of greenhouse gases such as $CH_4$ and $N_2O$ [6]. Additionally, the fertilizers applied to the crop fields can seep into groundwater, increase biochemical oxygen demand, and cause algal blooms by elevating the phosphorus content, with detrimental effects on aquatic ecosystems. Furthermore, as livestock manure can contain antibiotics and heavy metals, they can be transported to the soil crops when used as a fertilizer and eventually affect both livestock and human health via the food chain [7]. Though fertilization has been the conventional treatment of livestock manure as a facile process in the field, concerns are rising with regard to its aggravating impact on the environment, requesting endeavors to find more sustainable treatment options.

The conversion of livestock manure into biogas has garnered considerable interest, not only as a viable biological treatment for livestock manure but also as a means of recovering renewable energy. The collection of biogas produced during the treatment contributes to mitigate the greenhouse gas emissions that would otherwise be released into the atmosphere [8]. The biogas production of livestock manure is based on the decomposition of organic substances under anaerobic conditions, offering the advantage of preventing contamination from livestock manure, nutrient recovery, and composting [9]. The biogas consists of $CH_4$ and other impurities such as $CO_2$ and $H_2S$, meaning the subsequent purification step is required to enhance $CH_4$ content that can be used as a fuel for generating heat and electricity [10]. While biogas production from livestock manure has primarily been developed and implemented in European countries, Asian countries also possess promising potential for biogas generation from large-scale livestock farming industries [11]. However, biogas production presents certain limitations, including the comparatively extended treatment period, the supplementary expenses required for the subsequent purification, and the deliberate management for microorganisms [12,13]. The practical applicability of biogas production may be further constrained if impurities remain even after the purification [14].

Recently, solid fuel production through carbonization in an oxygen-free environment has drawn attention, primarily driven by the fundamental simplicity of the treatment process and the stability exhibited by the resulting product, which facilitates its long-term storage. Especially, this treatment is widely perceived as a significant step towards a carbon-neutral society, as it results in low carbon emissions during carbonization. Extensive investigations have been conducted on diverse organic wastes such as wastewater sludge [15–17], food debris [18,19], coffee grounds [20–22], aquatic organisms [23–25], grains, and fruit shells [26–29], yielding encouraging outcomes as a promising alternative for the conversion of organic waste into renewable energy sources. Solid fuel production from livestock manure has also been investigated [30,31]; however, more research is needed to establish solid fuel production as a sustainable treatment method for livestock manure, particularly regarding solid fuel quality improvements to possess sufficient heating values. Additionally, as livestock manure originally contains high moisture contents from its generation, how to reduce the moisture content from the livestock manure in a sustainable fashion is another obstacle to overcome to move solid fuel production via carbonization forward.

The major challenge of the carbonization lies in establishing economic feasibility, as the high energy consumption required for heating during the carbonization outweighs the enhanced heating value of the resulting product [32]. In order to minimize the energy consumption during the carbonization, a temperature of no more than 300 °C can be selected for the carbonization, referred to as torrefaction [33]. Furthermore, in order to enhance the heating value of the product, more consideration can be given to the selection of raw materials to maximize their inherent heating potential. To improve the heating value of the solid fuel derived from livestock manure, viable organic wastes that are combustible and practically accessible, for example, rice straw and sawdust, can be the targeted for co-torrefaction [34].

The objective of this study was to improve higher heating values by optimizing torrefaction temperatures and times for the solid fuel derived from livestock manure as well as mixing livestock manure with other organic wastes such as sawdust and rice straw. The torrefied solid fuel was compared with the solid fuel produced via simple drying to assess the feasibility of torrefaction in terms of solid fuel quality, especially on heating values.

## 2. Materials and Methods

### *2.1. Experimental Materials*

The cow manure obtained from a livestock farm in Goyang-si, Korea was investigated as the primary raw material for the solid fuel production process in this study. The collection was conducted in the summer season so that the moisture content of the livestock manure was relatively low compared to the values in other seasons. Additionally, sawdust and rice straw were adopted as the additives for the solid fuel production process (Figure 1). Prior to torrefaction, the sawdust was sieved to a size below 75 µm, and the rice straw sample was pulverized into fine particles using a blender. The particulate sawdust or rice straw was mixed with the cow manure. The characteristics of the materials in their original forms are shown in Table 1. The moisture content was measured by adding 2.5 g of the sample to a crucible and drying it at 105 °C for 24 h in a drying oven (C-DOD1, DaeyoungLab, Seoul, Korea). The dried sample was then placed in the muffle furnace (SH-FU-5MGE, SH Scientific, Sejong-si, Korea) and heated at 550 °C for 15 min, which was then cooled down to room temperature to measure fixed and volatile solids. The higher heating value was measured using a calorimeter (6100 Compensated Calorimeter, Parr Instrument company, Moline, IL, USA).

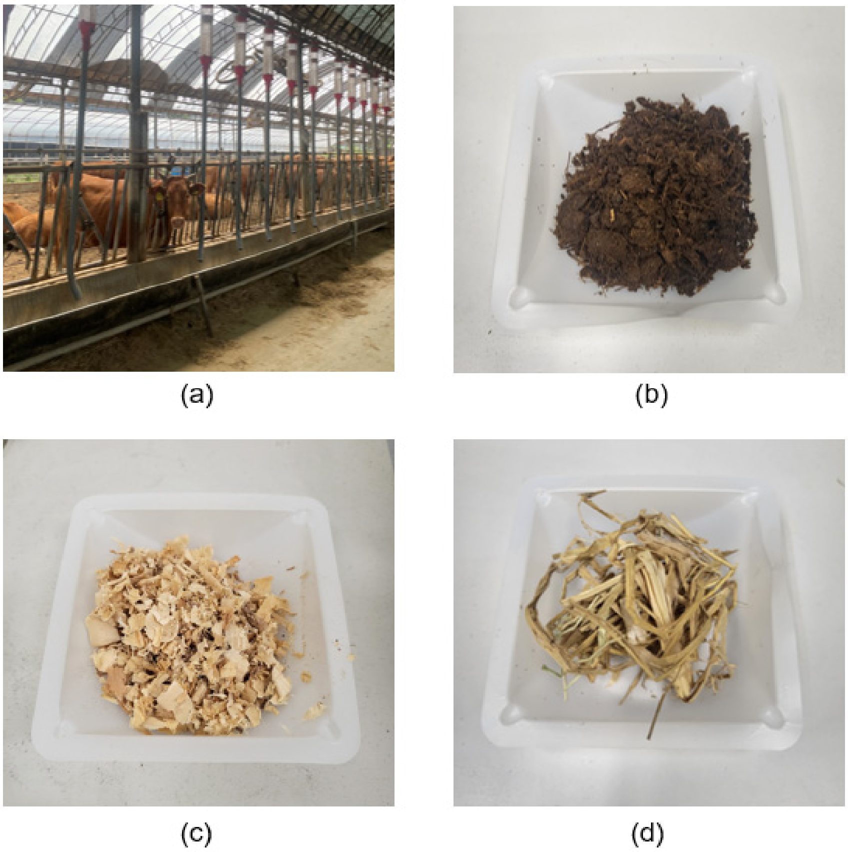

**Figure 1.** (**a**) Livestock farm site in Goyang-si, Korea; (**b**) cow manure, (**c**) sawdust, (**d**) and rice straw used in this study.

**Table 1.** Properties of cow manure, sawdust, and rice straw.

| | **Cow Manure** | **Sawdust** | **Rice Straw** |
|---|---|---|---|
| Moisture content (%) | 31.09 ± 2.19 | 9.47 ± 0.82 | 7.84 ± 0.09 |
| Volatile solids (%) | 23.62 ± 3.29 | 6.56 ± 2.04 | 23.99 ± 3.17 |
| Fixed solids (%) | 40.78 ± 1.65 | 83.96 ± 0.67 | 68.11 ± 3.78 |
| HHV [1] (kcal/kg) | 2168.65 ± 18.2 | 4322.78 ± 29.18 | 3562.54 ± 62.58 |

[1] Higher heating value.

*2.2. Solid Fuel Preparation*

Solid fuels were produced through either drying or torrefaction. For the drying process, 20 g of the sample was dried at 105 °C for 24 h using a drying oven. The dried cow manure, sawdust, and rice straw were named as DM (dry manure), DS (dry sawdust), and DR (dry rice straw), respectively. For the torrefaction process, 20 g of the sample was placed in the combustion boat (ULCB005, LK LabKorea, Gyeonggi-do, Korea), which was then placed in the center of a tubular electric furnace (PTF-1203, U1TECH, Gyeonggi-do, Korea). During the torrefaction, high purity nitrogen gas (Purity > 99.999%, Seoul specialty gases Co., Seoul, Korea) was kept flowing at a constant flow rate of 2 L/min in the furnace. Torrefaction was conducted under varying temperatures of 200, 250, and 300 °C as well as torrefaction times of 20, 30, and 40 min, respectively. The carbonized samples were named as carbonized manure (CM), carbonized sawdust (CS), and carbonized rice straw (CR), followed by the torrefaction temperature and time. The solid fuel was in the form of a dried or torrefied blend of materials without palletization and compaction.

In the case of mixing materials, cow manure was mixed with sawdust or rice straw in a blender at various ratios from 1:1 to 10:1. The mixed samples were also either dried or torrefied and named as dry manure with sawdust (DMS), dry manure with rice straw (DMR), carbonized manure with sawdust (CMS), and carbonized manure with rice straw (CMR), respectively.

*2.3. Characterization of Solid Fuel*

The solid fuels produced were analyzed for their characteristics by measuring the moisture content, ash content, volatile content, higher heating value (HHV), and elemental composition. The moisture content was determined using a moisture analyzer (MB90, OHAUS, Parsippany, NJ, USA). The volatile content was analyzed by igniting the dried sample at 950 °C for 7 min in a muffle furnace and cooling down to room temperature, followed by the calculation of the sample weight difference before and after the ignition. The ash content was analyzed in the same way as the volatile content, except with heating the sample at 550 °C for 120 min in the muffle furnace. The fixed carbon content was calculated as below.

$$\text{Fixed carbon (\%)} = 100 - \text{moisture content (\%)} - \text{ash content (\%)} - \text{volatile content (\%)}$$

The higher heating value (kcal/kg) and the elemental composition (C, H, N, S, O) were analyzed using a calorimeter and an elemental analyzer (Flash2000, Thermo Fisher Scientific, Waltham, MA, USA), respectively.

Mass yields in the drying process and the torrefaction process were calculated with the following equation.

$$\text{Mass yield (\%)} = \frac{M_f}{M_i} \times 100$$

where $M_i$ is the mass before drying or torrefaction, and $M_f$ is the mass after drying or torrefaction. Additionally, energy density was calculated as below.

$$\text{Energy density} = \frac{HHV_f}{HHV_i}$$

where $HHV_i$ is the HHV of raw material, and $HHV_f$ is the HHV of the dried or torrefied material.

## 3. Results

*3.1. Effects of Torrefaction Temperature and Time*

Table 2 shows the results of the carbonized cow manure (CM) and carbonized cow manure mixed with sawdust at a 1:1 ratio (CMS) and rice straw at a 1:1 ratio (CMR) under different torrefaction temperatures and times. When cow manure was carbonized at 300 °C and 30 min, the mass yield decreased by 22.4% compared to 200 °C, increasing the ash content and decreasing the volatile content, resulting in a fixed carbon increase of 6.25%. Similarly, the mass yield of CMS gradually decreased from 79.95% to 52.8% as the torrefaction temperature increased from 200 °C to 300 °C, with a gradual increase in the ash content and a decrease in the volatile content leading to the increase in the fixed carbon by 16.46%. The CMR showed similar results to the cases of the CM and CMS; the mass yield decreased from 76.69% to 50.33%, the ash increased from 20.45% to 31.51%, the volatile content decreased from 73.66% to 52.3%, and the fixed carbon increased from 4.55% to 15.01% as the torrefaction temperature increased. At a torrefaction temperature of 300 °C, the fixed carbon values of the CM, CMS, and CMR increased over the torrefaction time. Overall, the increase in both the torrefaction temperature and time led to the increase in the fixed carbon, which would be favorable in the solid fuel quality. However, as the energy consumption for the torrefaction should be saved as much as possible for economic feasibility, the examination of the solid fuel quality based on the heating value is also desirable.

**Table 2.** Proximate analysis of carbonized cow manure, cow manure with sawdust, and cow manure with rice straw according to the test conditions.

| Sample | Temp. (°C) | Time (min) | Mass Yield (%) | Moisture (%) | Ash (%) | Volatile (%) | Fixed Carbon (%) |
|---|---|---|---|---|---|---|---|
| CM | 200 | 30 | 64.04 | 1.78 ± 1.21 | 28.69 ± 0.11 | 69.22 ± 3.00 | 0.31 |
| | 250 | 30 | 64.47 | 1.8 ± 0.76 | 28.65 ± 0.31 | 69.42 ± 0.95 | 0.12 |
| | 300 | 30 | 52.30 | 1.39 ± 0.41 | 39.21 ± 0.82 | 52.83 ± 1.60 | 6.56 |
| | 300 | 20 | 56.10 | 1.99 ± 0.12 | 36.22 ± 0.11 | 58.22 ± 2.76 | 3.57 |
| | 300 | 40 | 46.43 | 1.36 ± 0.99 | 42.71 ± 0.14 | 44.10 ± 0.92 | 11.83 |
| CMS (1:1) | 200 | 30 | 79.95 | 2.1 ± 0.3 | 11.12 ± 0.49 | 79.28 ± 2.27 | 7.51 |
| | 250 | 30 | 76.62 | 1.47 ± 0.53 | 11.73 ± 0.49 | 71.80 ± 1.19 | 15.00 |
| | 300 | 30 | 52.80 | 2.02 ± 0.23 | 17.87 ± 0.11 | 56.14 ± 1.89 | 23.97 |
| | 300 | 20 | 55.46 | 2.34 ± 0.24 | 16.80 ± 0.08 | 65.78 ± 0.92 | 15.09 |
| | 300 | 40 | 51.52 | 2.23 ± 0.97 | 21.55 ± 0.26 | 47.29 ± 0.15 | 28.93 |
| CMR (1:1) | 200 | 30 | 76.69 | 1.34 ± 0.25 | 20.45 ± 0.39 | 73.66 ± 0.08 | 4.55 |
| | 250 | 30 | 74.52 | 1.9 ± 0.23 | 20.51 ± 0.001 | 71.29 ± 0.08 | 6.31 |
| | 300 | 30 | 50.33 | 1.18 ± 0.23 | 31.51 ± 0.69 | 52.30 ± 1.07 | 15.01 |
| | 300 | 20 | 49.21 | 1.08 ± 0.12 | 29.86 ± 0.33 | 59.61 ± 0.35 | 9.45 |
| | 300 | 40 | 48.99 | 1.04 ± 0.07 | 30.13 ± 0.67 | 49.98 ± 1.88 | 18.85 |

As shown in Figure 2, all of the samples tested in this study showed increases in heating values as the temperature increased from 200 °C to 300 °C. The heating value increases in the CM, CMS, and CMR were 14.45%, 23.25%, and 13.53%, respectively. When the torrefaction time was increased from 20 min to 40 min, with the temperature fixed at 300 °C, the heating value was increased; however, the increase between 30 min and 40 min was not significant compared to the case of the temperature increase. When torrefied for 40 min, the CM, CMS, and CMR showed the highest heating values of 3785.2 kcal/kg, 4817.50 kcal/kg, and 4238.47 kcal/kg, respectively.

Based on the response surface analysis using Minitap, as shown in Figure 3, the heating value of CM was estimated a function of torrefaction temperature and time:

$$y = 3669 - 15.52\, x_1 + 51.2\, x_2 + 0.0403\, {x_1}^2 - 0.566\, {x_2}^2$$

where y is HHV (kcal/kg), $x_1$ is temperature (°C), and $x_2$ is time (min). Likewise, the equations for CMS and CMR are as below.

$$y = 5251 - 33.4\, x_1 + 102.8\, x_2 + 0.0873\, {x_1}^2 - 1.48\, {x_2}^2$$

$$y = 4431 - 30.6\, x_1 + 138.8\, x_2 + 0.0765\, {x_1}^2 - 2.21\, {x_2}^2$$

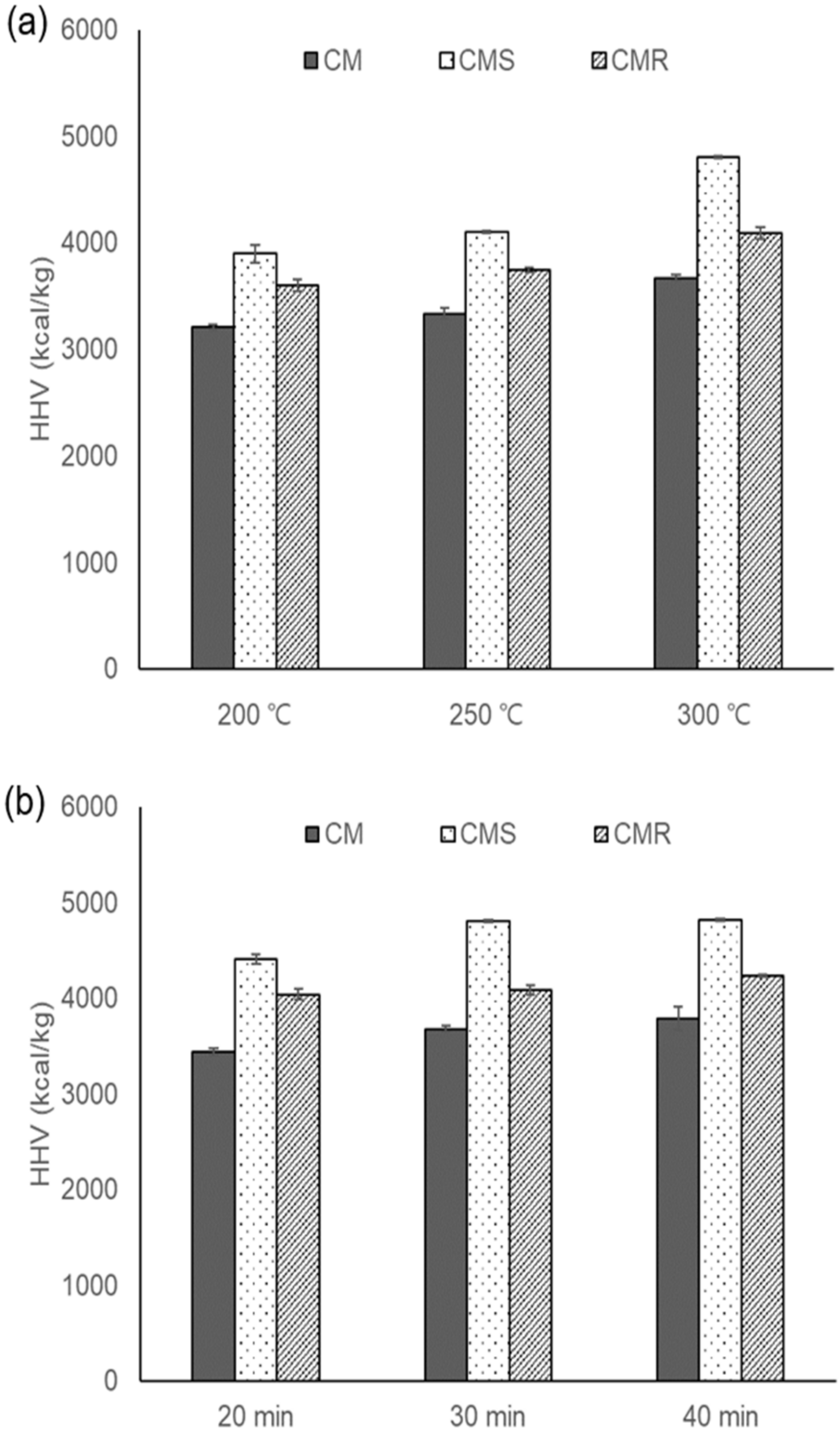


**Figure 2.** Higher heating values of CM, CMS, and CMR according to (**a**) carbonization temperature at 30 min and (**b**) carbonization time at 300 °C.

The estimated temperature and time for the highest heating values of the CM, CMS, and CMR were 300 °C, 40 min; 300 °C, 34.55 min; and 300 °C, 31.31 min, respectively. Considering the energy consumption during the torrefaction, 300 °C, 30 min was chosen as the optimum torrefaction condition in the following investigation.

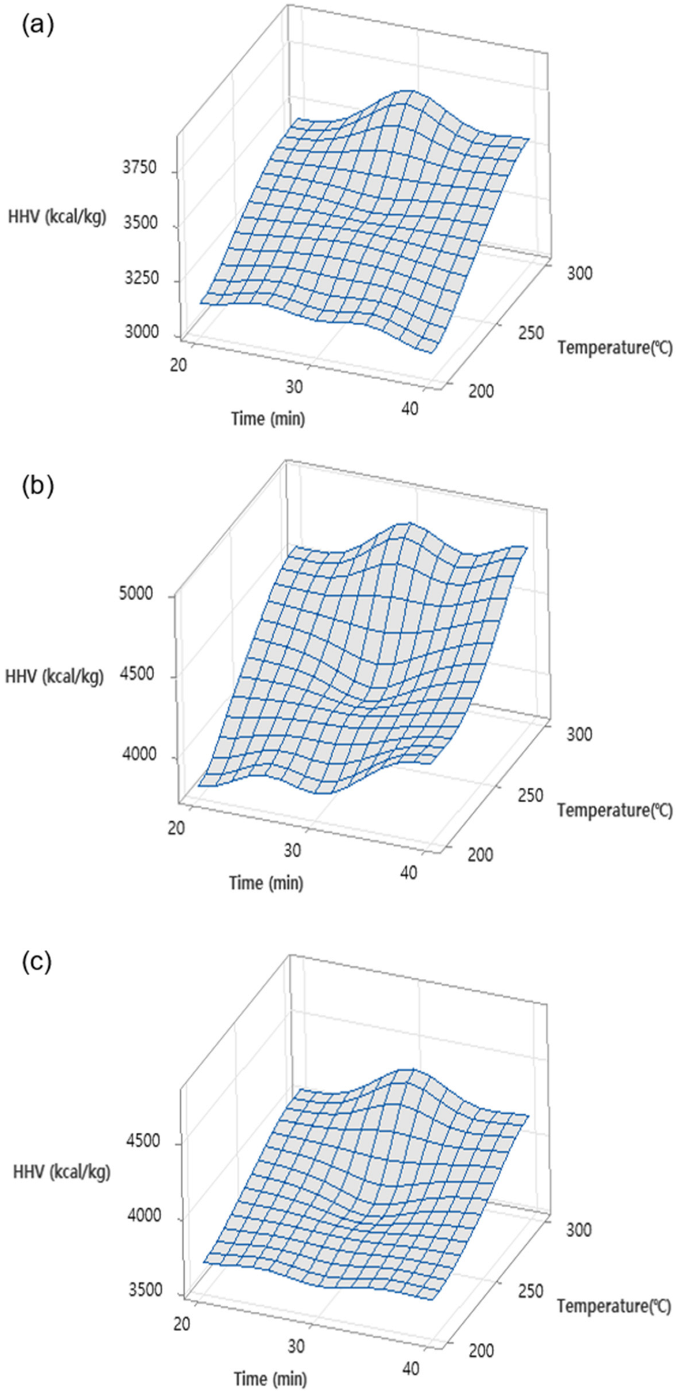


**Figure 3.** Response surface analysis of (**a**) CM, (**b**) CMS, and (**c**) CMR according to torrefaction temperature and time.

### *3.2. Effects of Mixing Ratio of Cow Manure with Sawdust or Rice Straw*

When the cow manure was mixed with sawdust or rice straw in the various mixing ratio, the mass yield of CMS and CMR was not significantly affected by the mixing ratio (Table 3). However, ash content increased with an increase in the cow manure content, whereas volatile content decreased (Tables 4 and 5). In case of CMS an CMR, the fixed carbon was highest (23.97% and 13.77%) at a 1:1 mixing ratio, then tended to decrease to 9.5% and 8.01% at a 10:1 mixing ratio, respectively. This result indicated that the higher cow manure content led to higher ash content, even without the noticeable mass yield change, which would be undesirable for the solid fuel quality.

**Table 3.** Mass yield of CMS and CMR (test condition: 300 °C, 30 min) under varying mixing ratios (increase in ratio indicates the increase in cow manure content).

| Mixing Ratio | 1:1 | 2:1 | 3:1 | 5:1 | 6:1 | 10:1 |
|---|---|---|---|---|---|---|
| CMS | 52.8 ± 9.01% | 53.98 ± 1.94% | 50.68 ± 1.17% | 51.06 ± 0.58% | 52.69 ± 0.55% | 51.67 ± 0.60% |
| CMR | 50.58 ± 4.68% | 49.93 ± 2.17% | 52.66 ± 0.58% | 52.44 ± 1.45% | 51.47 ± 0.39% | 49.83 ± 0.66% |

**Table 4.** Proximate analysis of CMS (test condition: 300 °C, 30 min) under varying mixing ratios.

| Mixing Ratio | 1:1 | 2:1 | 5:1 | 10:1 |
|---|---|---|---|---|
| Moisture | 2.02 ± 0.23 | 0.85 ± 0.04 | 1.95 ± 0.34 | 1.39 ± 0.61 |
| Ash | 17.87 ± 0.11 | 26.74 ± 0.22 | 32.10 ± 0.85 | 36.10 ± 0.68 |
| Volatile | 56.14 ± 1.89 | 56.12 ± 3.89 | 53.10 ± 2.35 | 53.10 ± 1.29 |
| Fixed carbon | 23.97 | 16.29 | 12.06 | 9.50 |

**Table 5.** Proximate analysis of CMR (test condition: 300 °C, 30 min) under varying mixing ratios.

| Mixing Ratio | 1:1 | 2:1 | 5:1 | 10:1 |
|---|---|---|---|---|
| Moisture | 1.29 ± 0.15 | 1.90 ± 0.62 | 1.27 ± 0.71 | 1.39 ± 0.36 |
| Ash | 27.78 ± 0.54 | 32.27 ± 0.31 | 35.99 ± 0.65 | 38.96 ± 0.47 |
| Volatile | 57.17 ± 0.15 | 55.06 ± 0.48 | 53.34 ± 0.11 | 51.64 ± 0.78 |
| Fixed carbon | 13.77 | 10.77 | 9.40 | 8.01 |

Figure 4 shows the trend in heating values and moisture contents according to the mixing ratio. The moisture content before the torrefaction gradually increased as the ratio of cow manure increased in both the CMS and CMR. As the cow manure ratio increased from 1:1 to 10:1, the heating value of CMS decreased from 4810.85 kcal/kg to 3687.63 kcal/kg. Similarly, the heating value of the 1:1 ratio of the CMR was 4324.84 kcal/kg, and the heating value decreased to 3523.04 kcal at the 10:1 ratio. Such a trend was also observed in the calculated heating value based on the CM, CS, and CR heating values. The slight deviation was found as the mixing ratio moved away from 1:1, probably due to some of the heat used for the moisture vaporization. Though the best material for the torrefied solid fuel was sawdust, based on the results obtained in this study, the further test with the mixing ratio lower than 1:1 was not conducted since the practical supply of sawdust would not be over the cow manure generation.

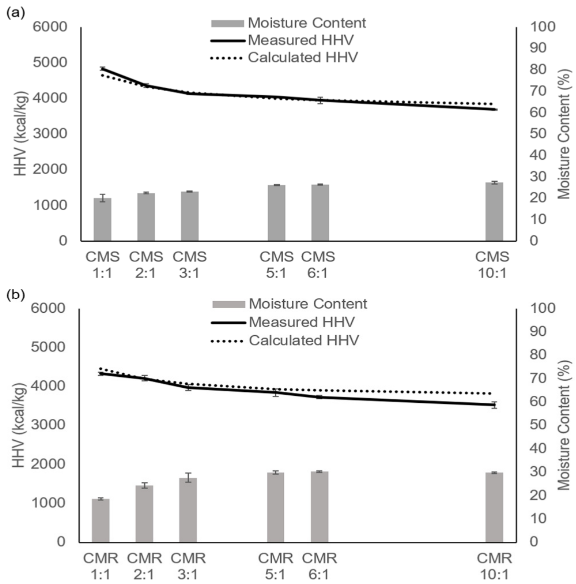


**Figure 4.** Effect of mixing ratio on HHV and moisture content of (**a**) CMS and (**b**) CMR.

### 3.3. Comparison of Simple Drying and Torrefaction

Table 6 summarizes the differences in solid fuel properties between simple drying and torrefaction. It turned out that the torrefaction process resulted in higher ash content and a lower volatile content compared to the drying process. Additionally, the fixed carbon content in the solid fuel was higher in the torrefaction process. As shown in Figure 5, the torrefaction process showed higher heating values than the drying process. Overall, the results suggested that the torrefaction process was more effective in producing solid fuel with higher fixed carbon content and heating value compared to the simple drying process.

**Table 6.** Proximate analysis of dried and carbonized cow manure, sawdust, rice straw, cow manure with sawdust, and cow manure with rice straw (test condition: 300 °C and 30 min).

| Sample | Mass Yield (%) | Moisture (%) | Ash (%) | Volatile (%) | Fixed Carbon (%) |
|---|---|---|---|---|---|
| DM | 69.17 | 3.71 ± 0.34 | 28.57 ± 0.40 | 67.43 ± 0.76 | 0.47 |
| CM | 52.3 | 1.39 ± 0.41 | 39.21 ± 0.82 | 52.83 ± 1.60 | 6.56 |
| DS | 84.11 | 1.25 ± 0.1 | 0.82 ± 0.03 | 88.29 ± 0.28 | 9.65 |
| CS | 62.11 | 2.00 ± 0.28 | 0.98 ± 0.002 | 82.91 ± 0.11 | 14.11 |
| DR | 79.48 | 3.16 ± 0.43 | 10.79 ± 1.75 | 85.78 ± 0.45 | 0.27 |
| CR | 54.34 | 2.83 ± 0.42 | 20.49 ± 0.15 | 59.04 ± 0.42 | 17.64 |
| DMS | 82.13 | 2.23 ± 0.12 | 13.34 ± 0.11 | 76.56 ± 0.25 | 7.86 |
| CMS | 52.8 | 2.02 ± 0.23 | 17.87 ± 0.11 | 56.14 ± 1.89 | 23.07 |
| DMR | 81.08 | 2.39 ± 0.06 | 20.05 ± 0.03 | 73.22 ± 0.19 | 4.34 |
| CMR | 49.06 | 0.91 ± 0.14 | 29.71 ± 0.22 | 50.39 ± 0.64 | 18.99 |

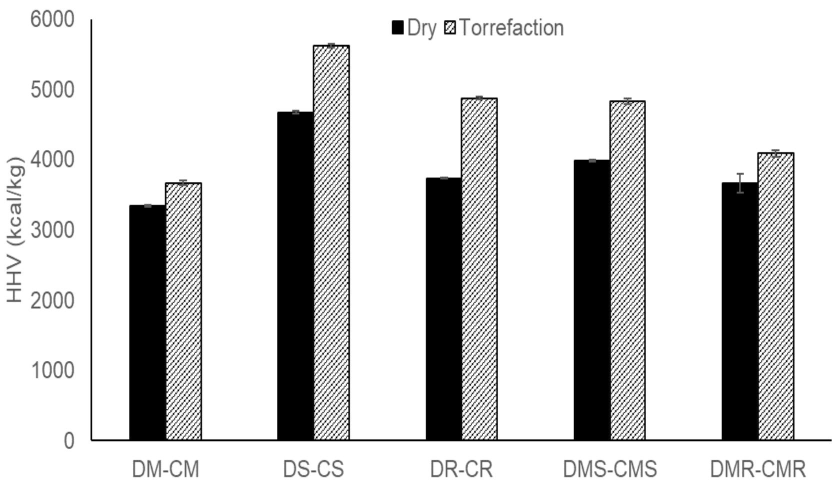


**Figure 5.** Comparison of dried and torrefaction samples in terms of HHV (test condition: 300 °C and 30 min). Note that the torrefaction was carried out without drying in this study since the original moisture content of the cow manure was affordable for the torrefaction without heat pretreatment.

Figure 6 highlights the difference in the energy density between the dried and torrefied solid fuels. All of the samples, including the mixture of cow manure and sawdust (MS), cow manure and rice straw (MR), unmixed cow manure, sawdust, and rice straw, show higher energy densities when torrefied than dried. Specifically, the torrefied samples possessed energy density increases of 69.18% for CM, 30.12% for CS, 36.83% for DR, and 20.52% and 11.47% for CMS and CMR, respectively. Energy density was the highest in CM, due to the lowest HHV value (2168.65 kcal/kg) in the raw material, subsequently leading to the higher increase rate of HHV with the solid fuel formed. The energy density growth rate between drying and torrefaction was the highest with the unmixed rice straw, showing as 30.44% higher in CR than in DR. In the case of the mixed samples of manure and sawdust and manure and rice straw, about 2.76% and 9.35% increases in energy densities were observed with torrefaction. Though the mixed sample of manure and organic waste resulted in a higher HHV, the increase in the energy density was insignificant due to the high HHV of the original materials. Based on these results, combustible additives such as sawdust and rice straw can directly improve the HHV of the solid fuel via co-torrefaction; however, the enhancement in the energy density would not be as much as HHV.

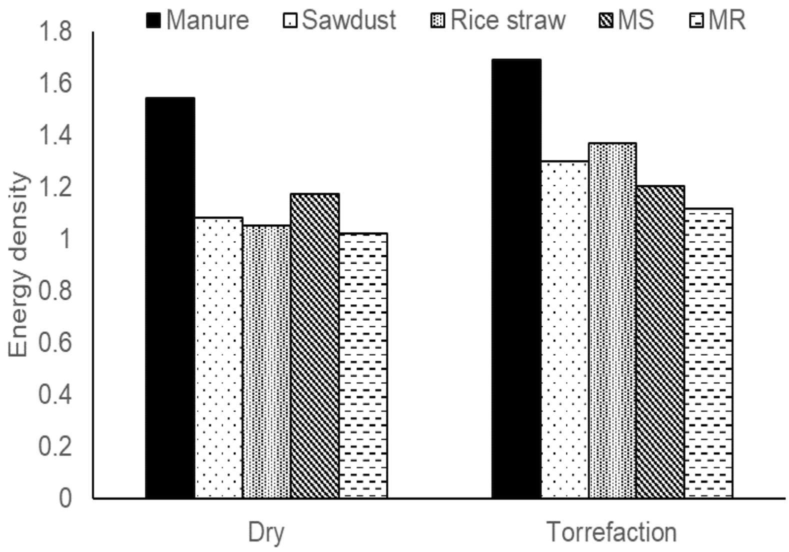


**Figure 6.** Comparison of dried and torrefaction samples in terms of energy density (test condition: 300 °C and 30 min).

Figure 7 shows the selected solid fuel quality on a val Krevelen diagram. While the dried cow manure remained in the biomass region, the torrefied cow manure moved towards the peat region. Additionally, the cow manure mixed with rice straw via torrefaction became more coalized and reached the lignite zone. The results suggest that the torrefaction process had a significant effect on the conversion of cow manure to quality solid fuel. Further investigation on the coalization process could support the development of more efficient and cost-effective solid fuel production methods.

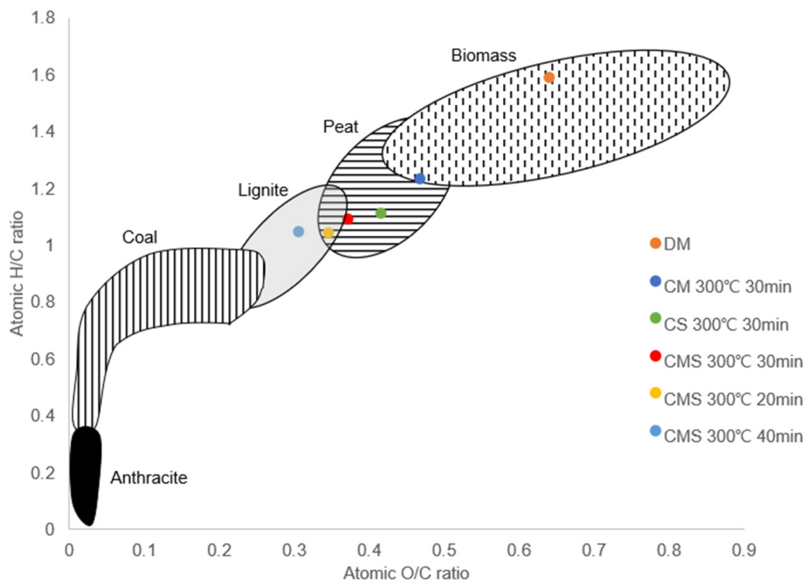


**Figure 7.** Solid fuel quality of selected samples on the van Krevelen diagram.

Though the solid fuel production of cow manure via torrefaction would be favorable in terms of heating values as well as shorter processing times than drying, the economic feasibility is still an issue for application on a field scale. The energy input for the heating and the consumption of nitrogen gas during torrefaction should be compensated by the condensed energy formed and the fixed carbon. Therefore, it is important to conduct further research to develop more sustainable and economically feasible methods for solid fuel production through torrefaction, as this solid fuel production presents a substantial potential for the management of livestock manure if practically available.

Another critical point to obtain high-quality solid fuel is to utilize livestock manure when it is as fresh as possible. In this study, it was found that the heating value of the cow manure decreased from 3669 kcal/kg to 2321 kcal/kg as the storage period reached almost 6 months. As carbon loss to the atmosphere due to microbial degradation might be inevitable without torrefaction, rapid collection upon livestock excretion and immediate torrefaction is desirable to enhance the heating value. Otherwise, the variations in the storage conditions, such as temperature control, should be further investigated to keep as much of the carbon in the livestock manure as possible.

## 4. Conclusions

Cow manure with and without sawdust and rice straw has been successfully converted to solid fuel via torrefaction. The increase in the torrefaction temperature from 200 °C to 300 °C and a torrefaction time from 20 min to 40 min resulted in the noticeable increase in fixed carbon and heating values. The optimal torrefaction temperature and times for the CM, CMS, and CMR were determined to be 300 °C and 40, 34.55, and 31.31 min, respectively, based on the highest heating value.

The mixture of cow manure and sawdust or rice straw showed a decrease in fixed carbon contents and heating values as the cow manure contents increased. Solid fuel produced through torrefaction had higher fixed carbon contents and heating values than solid fuel produced through the drying process. Overall, cow manure was converted into higher quality solid fuel, as it was processed via torrefaction, and this was mixed with the additives of higher heating values. Further studies on economic feasibility and storage effects are necessary to prove that solid fuel production via torrefaction is a sustainable waste treatment process.

This study demonstrated torrefaction as more than just a waste-to-energy conversion process, implying its potential as a carbon capture and storage process. The increase in the fixed carbon content, as well as the heating value as a result of torrefaction, supported the prospective use of torrefaction as a means of carbon sequestration. With the increasing demand of low carbon emissions, torrefaction is expected to draw more attention as a process towards a carbon-neutral society, as well as a circular economy.

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## References


1. Iwuozor, K.O.; Emenike, E.C.; Aniagor, C.O.; Iwuchukwu, F.U.; Ibitogbe, E.M.; Okikiola, T.B.; Omuku, P.E.; Adeniyi, A.G. Removal of pollutants from aqueous media using cow dung-based adsorbents. *Curr. Res. Green Sustain. Chem.* **2022**, *5*, 100300. [CrossRef]
2. Yuvaraj, A.; Thangaraj, R.; Ravindran, B.; Woong, S.; Karmegam, N. Centrality of cattle solid wastes in vermicomposting technology e A cleaner resource recovery and biowaste recycling option for agricultural and environmental sustainability. *Environ. Pollut.* **2021**, *268*, 115688. [CrossRef]
3. Ministry of Agriculture, food and Rural Affairs. Survey on Livestock Manure. 2023. Available online: https://www.korea.kr/briefing/pressReleaseView.do?newsId=156559757 (accessed on 31 May 2023).
4. Liu, W.; Zeng, D.; She, L.; Su, W.; He, D.; Wu, G.; Ma, X.; Jiang, S.; Jiang, C.; Ying, G. Science of the Total Environment Comparisons of pollution characteristics, emission situations, and mass loads for heavy metals in the manures of different livestock and poultry in China. *Sci. Total Environ.* **2020**, *734*, 139023. [CrossRef] [PubMed]
5. Font-Palma, C. Methods for the Treatment of Cattle Manure—A Review. *C* **2019**, *5*, 27. [CrossRef]
6. Oshita, K.; Toda, S.; Takaoka, M.; Kanda, H.; Fujimori, T.; Matsukawa, K.; Fujiwara, T. Solid fuel production from cattle manure by dewatering using liquefied dimethyl ether. *Fuel* **2015**, *159*, 7–14. [CrossRef]
7. Leclerc, A.; Laurent, A. Framework for estimating toxic releases from the application of manure on agricultural soil: National release inventories for heavy metals in 2000–2014. *Sci. Total Environ.* **2017**, *590–591*, 452–460. [CrossRef]
8. Reinelt, T.; Delre, A.; Westerkamp, T.; Holmgren, M.A.; Liebetrau, J.; Scheutz, C. Comparative use of different emission measurement approaches to determine methane emissions from a biogas plant. *Waste Manag.* **2017**, *68*, 173–185. [CrossRef]
9. Batzias, F.A.; Sidiras, D.K.; Spyrou, E.K. Evaluating livestock manures for biogas production: A GIS based method. *Renew. Energy* **2005**, *30*, 1161–1176. [CrossRef]
10. Nasir, I.M.; Mohd Ghazi, T.I.; Omar, R. Anaerobic digestion technology in livestock manure treatment for biogas production: A review. *Eng. Life Sci.* **2012**, *12*, 258–269. [CrossRef]
11. Ali, M.M.; Ndongo, M.; Bilal, B.; Yetilmezsoy, K.; Youm, I.; Bahramian, M. Mapping of biogas production potential from livestock manures and slaughterhouse waste: A case study for African countries. *J. Clean. Prod.* **2020**, *256*, 120499. [CrossRef]
12. Neshat, S.A.; Mohammadi, M.; Najafpour, G.D.; Lahijani, P. Anaerobic co-digestion of animal manures and lignocellulosic residues as a potent approach for sustainable biogas production. *Renew. Sustain. Energy Rev.* **2017**, *79*, 308–322. [CrossRef]
13. Lim, B.R.; Lee, K.; Noh, S.Y.; Park, K.Y. Characteristics of Microalgal Growth on Anaerobic Effluent of Animal Waste. *J. Korean Soc. Water Qual.* **2008**, *24*, 306–310.
14. Bagher, A.M. Advantages and disadvantages of biogas energy. *Bull. Adv. Sci. Res.* **2015**, *1*, 132–135.
15. Zhao, P.; Shen, Y.; Ge, S.; Yoshikawa, K. Energy recycling from sewage sludge by producing solid biofuel with hydrothermal carbonization. *Energy Convers. Manag.* **2014**, *78*, 815–821. [CrossRef]
16. Kim, D.; Lee, K.; Park, K.Y. Hydrothermal carbonization of anaerobically digested sludge for solid fuel production and energy recovery. *Fuel* **2014**, *130*, 120–125. [CrossRef]
17. Xu, Z.X.; Song, H.; Li, P.J.; He, Z.X.; Wang, Q.; Wang, K.; Duan, P.G. Hydrothermal carbonization of sewage sludge: Effect of aqueous phase recycling. *Chem. Eng. J.* **2020**, *387*, 123410. [CrossRef]
18. Papanikola, K.; Papadopoulou, K.; Tsiliyannis, C.; Fotinopoulou, I.; Katsiampoulas, A.; Chalarakis, E.; Georgiopoulou, M.; Rontogianni, V.; Michalopoulos, I.; Mathioudakis, D.; et al. Food residue biomass product as an alternative fuel for the cement industry. *Environ. Sci. Pollut. Res.* **2019**, *26*, 35555–35564. [CrossRef]
19. Liu, H.; Ma, X.; Li, L.; Hu, Z.F.; Guo, P.; Jiang, Y. The catalytic pyrolysis of food waste by microwave heating. *Bioresour. Technol.* **2014**, *166*, 45–50. [CrossRef]
20. Nepal, R.; Kim, H.J.; Poudel, J.; Oh, S.C. A study on torrefaction of spent coffee ground to improve its fuel properties. *Fuel* **2022**, *318*, 123643. [CrossRef]
21. Kang, S.B.; Oh, H.Y.; Kim, J.J.; Choi, K.S. Characteristics of spent coffee ground as a fuel and combustion test in a small boiler (6.5 kW). *Renew. Energy* **2017**, *113*, 1208–1214. [CrossRef]
22. Kim, D.; Lee, K.; Bae, D.; Park, K.Y. Characterizations of biochar from hydrothermal carbonization of exhausted coffee residue. *J. Mater. Cycles Waste Manag.* **2017**, *19*, 1036–1043. [CrossRef]
23. Soroush, S.; Ronsse, F.; Verberckmoes, A.; Verpoort, F.; Park, J.; Wu, D.; Heynderickx, P.M. Production of solid hydrochar from waste seaweed by hydrothermal carbonization: Effect of process variables. *Biomass Convers. Biorefinery* **2022**. [CrossRef]
24. Jang, D.H. Moon Surface Analysis and Heavy Metal Adsorption Evaluation of Chemically Modified Biochar Derived from Starfish (*Asterina pectinifera*). *J. Korean Soc. Water Environ.* **2022**, *38*, 82–94.
25. Lee, J.; Lee, K.; Sohn, D.; Kim, Y.M.; Park, K.Y. Hydrothermal carbonization of lipid extracted algae for hydrochar production and feasibility of using hydrochar as a solid fuel. *Energy* **2018**, *153*, 913–920. [CrossRef]
26. Garba, M.U.; Moritiwon Oloruntoba, J.; Isah, A.G.; Alhassan, M. Production of Solid Fuel From Rice Straw Through Torrefaction Process. *Int. J. Sci. Eng. Investig.* **2014**, *4*, 37.
27. Chen, X.; Lin, Q.; He, R.; Zhao, X.; Li, G. Hydrochar production from watermelon peel by hydrothermal carbonization. *Bioresour. Technol.* **2017**, *241*, 236–243. [CrossRef] [PubMed]
28. Sabio, E.; Álvarez-Murillo, A.; Román, S.; Ledesma, B. Conversion of tomato-peel waste into solid fuel by hydrothermal carbonization: Influence of the processing variables. *Waste Manag.* **2016**, *47*, 122–132. [CrossRef]

29. Lee, J.; Jeong, E.; Lee, J.; Lee, Y.-G.; Chon, K. Comparative Evaluation of Methylene Blue and Humic Acids Removal Efficiency Using Rice Husk Derived Biochars and Powdered Activated Carbon. *J. Korean Soc. Water Environ.* **2021**, *37*, 483–492.
30. Dai, L.; Tan, F.; Wu, B.; He, M.; Wang, W.; Tang, X.; Hu, Q.; Zhang, M. Immobilization of phosphorus in cow manure during hydrothermal carbonization. *J. Environ. Manag.* **2015**, *157*, 49–53. [CrossRef] [PubMed]
31. Toufiq Reza, M.; Freitas, A.; Yang, X.; Hiibel, S.; Lin, H.; Coronella, C.J. Coronella Hydrothermal Carbonization (HTC) of Cow Manure: Carbon and Nitrogen Distributions in HTC Products. *Am. Inst. Chem. Eng.* **2016**, *35*, 1002–1011. [CrossRef]
32. Cahyanti, M.N.; Doddapaneni, T.R.K.C.; Kikas, T. Biomass torrefaction: An overview on process parameters, economic and environmental aspects and recent advancements. *Bioresour. Technol.* **2020**, *301*, 122737. [CrossRef] [PubMed]
33. Butler, J.W.; Skrivan, W.; Lotfi, S. Identification of Optimal Binders for Torrefied Biomass Pellets. *Energies* **2023**, *16*, 3390. [CrossRef]
34. Waheed, A.; Naqvi, S.R.; Ali, I. Co-Torrefaction Progress of Biomass Residue/Waste Obtained for High-Value Bio-Solid Products. *Energies* **2022**, *15*, 8297. [CrossRef]