Characteristics of Miscanthus Fuel by Wet Torrefaction on Fuel Upgrading and Gas Emission Behavior

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Abstract: Biomass is a solid fuel that can be used instead of coal to address the issue of greenhouse gases. Currently, biomass is used directly in combustion or via co-combustion in coal-fired power plants. However, its use is limited due to calorific value and ash problems. In this study, wet torrefaction (WT) was carried out at various temperatures (160 °C, 180 °C, and 200 °C) and the properties of the product were evaluated. In comparison to dry torrefaction, the ash contained in biomass was extracted by an acidic solution (i.e., acetic acid) from the overreaction of the biomass. From examining the ash content of the treated WT, it was confirmed that K₂O of basic ash was mainly extracted. In particular, in the case of K₂O, since the main cause of combustion problems are issues such as fouling and slagging, the removed WT can be stably combusted in the boiler. Finally, the combustion and emission behaviors were evaluated by TGA-DTG and TGA-FTIR. As the fuel-N was decreased in the WT process, the NOx in the emission gas after combustion was lower than that of raw miscanthus, and SO₂ showed a similar value. As a result, it was confirmed that the WT sample is an advanced fuel in terms of fuel upgrading, alkali minerals, and NOx emission compared to raw miscanthus.

Keywords: wet torrefaction; miscanthus; biomass; upgrading fuel; combustion

1. Introduction

Coal has been a major source of electricity for many decades. However, as air pollutants such as carbon dioxide (CO₂) and particulate matter (PM), which are generated from coal burning, have become a social issue, the proportion of coal is gradually decreasing [1,2]. In Korea, the Renewable Portfolio Standard (RPS) has been used since 2012, and plants with more than 500 MW of power are required to cover a certain percentage of the output with renewable energy. Therefore, in Korea, there has been considerable investment in renewable energy, such as solar, wind power, and biomass, and among them, the use of biomass as such wood pellets is mainly utilized [3–5]. As biomass grows, it absorbs CO₂ from the atmosphere. Of the absorbed CO₂, carbon remains in the biomass, and only the O₂ is discharged. For this reason, CO₂ emitted by burning biomass is CO₂ due to carbon in biomass, so CO₂ recycling is possible [6,7]. If a biomass power plant is not newly constructed and existing coal-fired power plants are used as they are, it is economical compared to newly constructed solar and wind power [8,9].

Biomass is divided into lignocellulosic and herbaceous biomass according to the carbon component and life cycle. Both are highly utilized in terms of CO₂ recycling, but in terms of deforestation and low production cost, herbaceous biomass is more advantageous than lignocellulosic biomass [10]. Biomass
can be utilized into (1) a co-combustion type that burns a certain amount of biomass and coal together, and (2) a direct combustion method that burns only biomass fuel alone. In the case of biomass power generation, there is an advantage that a dedicated grinder or power generation system can be operated according to the fuel because new facilities are being constructed and operated. However, the biomass fuels used in Korea are mixed at 3%~5% in coal-fired power plants, and the mixing rate cannot be increased due to problems such as milling and calorific value [11–13]. Many researchers have studied torrefaction technology for the purpose of improving the calorific value and the milling.

Ru et al. performed torrefaction for 30 min at a temperature of 200–300 °C using poplar and compared the physicochemical properties based on the treatment temperature. After comparing the poplar torrefaction yield, energy yield, mass energy density, and activation energy concluded that the operating conditions at 250 °C are the most efficient [14].

Arias et al. studied the effects of milling and reactivity on the torrefaction of woody biomass. Torrefaction process was operated with a residence time of 0–3 h at a temperature of 240–280 °C. As the temperature increased, the degree of milling increased and the reactivity decreased. Finally, the optimum operating conditions of mass loss (20%) and calorie increase (90%) were obtained at 240 °C for 30 min [15].

The technology removes moisture and volatile matter to within 10%. As the fixed carbon is increased by removing a portion of water and volatile matter, there is an advantage of increasing the calorific value effect. However, in addition to the fixed carbon, the content of ash is also relatively increased [16–18]. In order to complement the advanced dry torrefaction technique, the present study used wet torrefaction. The wet torrefaction can reduce alkali minerals such as K2O, Na2O among ash components. Accordingly, the wet torrefaction technology rather than the dry torrefaction can suppress clinker, fouling, and slugging phenomena when combusting in coal-fired power plants [19–21].

In this study, the pretreatment reactor (3L) was subjected to a temperature change of 160–200 °C to evaluate the properties of the produced fuel. Ash behavior was analyzed through XRF and X-ray maps, and combustion characteristics were compared on the basis of TGA-DTG results. Finally, post-combustion products (NO, SO2) were analyzed using TGA-FTIR equipment.

2. Materials and Methods

2.1. Wet Torrefaction Process

In this study, we used miscanthus sacchariflorus cultivated in Korea as biomass. The miscanthus was ground to a size of 50 mm or less, and the ratio of biomass-to-water for wet torrefaction was 1:10. The apparatus for wet torrefaction is shown in Figure 1. The wet torrefaction process is a method of supplying heat to the inside of the biomass with an electric furnace from the outside. It is also equipped with a K-type temperature sensor that can measure the temperature inside the reactor and the outer jacket. In the center of the reactor, a stirrer capable of mixing the reactants at a speed of up to 500 rpm is installed. In the wet torrefaction operating conditions of this study, the residence time was fixed at 1 h at the target temperature, and the product characteristics were analyzed according to the reaction temperatures of 160, 180, and 200 °C. When the wet torrefaction temperature is greater than 200 °C, the mass decomposition occurs largely because the decomposition of cellulose occurs together. Accordingly, in this study, a temperature of 200 °C or less was selected as a target and analyzed. In the case of a solid(miscanthus)-liquid(water) ratio, the flow between biomass and water is lowered when it is less than 10 times. When it is higher than 10 times, the amount of wastewater treatment increases when separating solid–liquid after the reaction. The wet torrefaction samples were dried in an oven at 105 °C for 24h and analyzed for fuel and combustion characteristics. The raw miscanthus was denoted as RM, and the wet torrefaction sample was denoted as WT-160, WT-180, and WT-200 according to the temperature. The detailed flow chart and mass balance of the wet torrefaction process is shown in Figure 2.
2.2. Analysis of the Wet Torrefaction Samples

A proximate analysis (TGA (thermogravimetric analyzer)-701, LECO Co., St. Joseph, MI, USA) that analyzes the fuel properties was carried out on the received basis, while elemental (TruSpec, LECO Co., St. Joseph, MI, USA) and sulfur analyses (SC-432DR, LECO Co., St. Joseph, MI, USA) were evaluated on a dry basis. For the calorific value, an AC600 device (LECO Co., St. Joseph, MI, USA) was used. In addition, a NREL analysis (NREL/TP-510-42618, TP-510-42623) was conducted to analyze the components of cellulose, hemicellulose, and lignin contained in biomass. In the case of ash in the biomass, it was prepared by maintaining the electric furnace at 700 °C for 6 h (ASTM, E1755-01), and the characteristics of the ash were examined with X-ray fluorescence equipment (XRF, Primus II,
RIGAKU Co.) and scanning electron microscope and x-ray spectroscopy (SEM and X-ray maps, S-4700, HITACHI). The melting point of the ash was measured in four sections (Initial Deformation Temperature (IDT), Softening Temperature (ST), Hemispherical Temperature (HT), and Fluid Temperature (FT)) using ASTM D1857. In addition, TG-DTG (Q500 TA) was used to show the combustion characteristics. Finally, the emission characteristics of the fuels were evaluated by TG-FTIR in conjunction with TGA.

3. Results and Discussion

3.1. Fuel Properties of WT Samples

Table 1 compares the proximate, ultimate analysis, atomic ratios, and calorific values for the fuel properties of a raw miscanthus (RM) that has been subjected to wet torrefaction (WT) pretreatment. The calorific value (Low Heating Value, LHV) of the WT samples increased by about 2.8–4 MJ/kg compared to the untreated RM. This result shows that the caloric value increased by the increase in the wet carbonization degree with an increasing treatment temperature (160–200 °C). Due to the increased wet carbonization degree of the WT samples, the moisture and ash content decreased, while the fixed carbon and volatile matter content relatively increased. In other words, the ultimate analysis showed that carbon (C) increased during pretreatment and that oxygen (O) and hydrogen (H), which are hydroxyl groups, decreased. When the results are expressed by the atomic ratio (H/C and O/C ratio), it can be seen that the ratio value gradually decreased as the pretreatment temperature increased. According to the literature [22], the higher the carbonization degree is, the lower the ratio of H/C and O/C will be. During the wet torrefaction process, dehydration, decarboxylation, and demethanation result in high quality fuel. In addition, the wet torrefaction resulted in an up to 61% reduction of ash contained in the biomass by using hot water at a high temperature and pressure compared to dry torrefaction [23]. The major components of the biomass are glucan, XMG (xylan, mannan and galactan), arabinan, and lignin, which are shown in Table 2. In the case of the untreated RM, the glucan was 41.77%, XMG was 21.74%, arabinan was 2.14%, and lignin was 16.80%. On the other hand, the WT samples showed that the constituents (XMG and arabinan) of hemicellulose with the lowest decomposition temperature decreased with an increasing temperature. The WT sample showed relatively increased glucan and lignin as the XMG and arabinan were extracted.

Table 1. Fuel characteristics of raw miscanthus (RM) and wet torrefaction (WT) samples.

| Contents         | Proximate Analysis (As Received Basis, wt %) | Ultimate Analysis (Dried Basis, wt %) | Atomic Ratio | HHV (As-Received Basis, MJ/kg) | LHV (As-Received Basis, MJ/kg) |
|------------------|---------------------------------------------|---------------------------------------|--------------|---------------------------------|--------------------------------|
| Raw Miscanthus (RM) | M. 8.18, V.M. 65.43, Ash 12.17, EC. 14.22, C 43.30, H 5.86, N 1.12, O 37.54, S 0.01 | C 1.62, H 0.65, O 15.38, S 14.03 |
| WT-160           | C 3.18, H 74.75, N 4.87, O 17.20, S 52.35, C 5.81, H 0.88, O 36.08, S 0.01 | C 1.35, H 0.51, O 18.15, S 16.87 |
| WT-180           | C 4.09, H 72.53, N 4.75, O 18.63, S 52.65, C 5.79, H 0.88, O 35.92, S 0.01 | C 1.33, H 0.51, O 18.78, S 17.49 |
| WT-200           | C 5.76, H 68.14, N 4.71, O 21.39, S 53.75, C 5.62, H 0.21, O 33.82, S 0.01 | C 1.25, H 0.47, O 19.28, S 18.01 |

RM: Raw Miscanthus; WT-160: Wet torrefaction sample at 160 °C; WT-180: Wet torrefaction sample at 180 °C; WT-200: Wet torrefaction sample at 200 °C.

Table 2. Carbohydrate analysis results of raw miscanthus (RM) and wet torrefaction (WT) samples.

| Contents         | Chemical Composition (Dry Basis, wt %) |
|------------------|---------------------------------------|
| Raw Miscanthus (RM) | Glucan 50.66, XMG (xylan+Mannan+Galactan) 26.37, Arabinan 2.60, Lignin 20.38 |
| WT-160           | Glucan 65.22, XMG 4.50, Arabinan - 30.28 |
| WT-180           | Glucan 65.25, XMG 2.30, Arabinan - 32.46 |
| WT-200           | Glucan 59.03, XMG - 40.97 |

RM: Raw Miscanthus; WT-160: Wet torrefaction sample at 160 °C; WT-180: Wet torrefaction sample at 180 °C; WT-200: Wet torrefaction sample at 200 °C.
3.2. Ash Composition of WT Samples

When the biomass is burned in coal-fired power plants, the ash contained in the biomass can be divided into fly ash in the form of small particles and bottom ash collected in the form of large particles [24]. Biomass has a higher K$_2$O content than coal, and the melting point of K$_2$O is about 740 $^\circ$C, which causes slagging and fouling problems during combustion in boilers [25]. In the case of the miscanthus used in this study, the miscanthus contained about 11% of K$_2$O (Table 3), and problems consequently occurred during combustion. In the case of simple dry torrefaction, the removal of water and some volatile matter led to an increase in the total ash ratio, which caused combustion problems. However, in the case of wet torrefaction, the ash tended to decrease, as shown in Table 1. In particular, it was confirmed that about 89% of ash reduced the content of K$_2$O. Basic minerals such as Na$_2$O, MgO, P$_2$O$_5$, K$_2$O, CaO, and MnO decreased while acidic minerals such as SiO$_2$, Al$_2$O$_3$, and TiO$_2$ increased. This is because while the hemicellulose in miscanthus decomposes during the wet torrefaction process, the XMG is overreacts and converts into an acidic solution such as formic acid, acetic acid, levulinic acid, 5-HMF, and furfural (Table 4). The converted acidic solution lowers the pH of the wet torrefaction liquid to 3.11 (WT-200), which extracts alkaline minerals from the miscanthus. As the basic ash with a low melting point was extracted, the initial deformation temperature (IDT) of the WT samples increased by 5.1% compared to RM (Table 5). That is, since the alkali-based minerals have a relatively low melting point, the melting point of the fuel lowers when the alkali-based minerals contain many minerals. In addition, the indicators of the effects of slagging and fouling on the effects of alkali-based minerals are shown in Table 5. All of these items such as the B/A ratio, silica percentage, fouling, and alkali index are all affected by alkali-based minerals, especially Na$_2$O and K$_2$O [26,27]. As described above, the WT sample was found to increase only the silica percentage and the remaining items decreased as the alkaline minerals were extracted. Additionally, from the SEM data shown in Figure 3, it can be seen that the raw miscanthus exhibited more scale on the surface than the WT-200 sample. In the X-ray maps, it was confirmed there was a lot of Si and K in addition to C and O. After treatment, the sample of WT-200 showed small X-ray map images of Si and K. As a result, the extracted alkali minerals contained in miscanthus during the wet torrefaction process can reduce the risk of slagging or fouling when the fuel is used in the power plant.

### Table 3. Mineral oxide contents of raw miscanthus (RM) and wet torrefaction (WT) samples.

| Contents          | Mineral Oxide (wt %) |
|-------------------|----------------------|
|                   | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | P$_2$O$_5$ | K$_2$O | CaO | TiO$_2$ | MnO | Fe$_2$O$_3$ |
| Raw Miscanthus (RM) | 0.30   | 1.77 | 5.88       | 74.08   | 1.87      | 11.09  | 2.78 | 0.43     | 0.30 | 1.51       |
| WT-160            | 0.11   | 0.41 | 7.10       | 89.77   | 0.08      | 1.12   | 0.23 | 0.53     | 0.02 | 0.63       |
| WT-180            | 0.10   | 0.40 | 6.92       | 89.38   | 0.11      | 1.17   | 0.26 | 0.61     | 0.03 | 1.02       |
| WT-200            | 0.13   | 0.59 | 8.48       | 86.89   | 0.07      | 1.17   | 1.18 | 0.54     | 0.03 | 0.92       |

### Table 4. Acid products analysis results of wet torrefaction liquid.

| Contents      | pH  | Formic Acid | Acetic Acid | Levulinic Acid | 5-HMF | Furfural |
|---------------|-----|-------------|-------------|----------------|-------|----------|
| WT-160-liquid | 4.06| 0.147       | 0.600       | 0.045          | 0.009 | 0.173    |
| WT-180-liquid | 3.41| 0.311       | 1.865       | 0.095          | 0.019 | 1.128    |
| WT-200-liquid | 3.11| 0.549       | 2.257       | 0.236          | 0.047 | 2.063    |
Table 5. IDT, Slagging and Fouling indices of raw miscanthus (RM) and wet torrefaction (WT) samples.

| Contents                  | Ash Fusion Temperature IDT (°C) | Slagging/Fouling Indices | B/A Ratio | Silica Percentage | Fouling Index | Alkali Index |
|---------------------------|--------------------------------|--------------------------|-----------|-------------------|---------------|--------------|
| Raw Miscanthus (RM)       | 1174                           |                          | 0.217     | 0.924             | 0.065         | 11.39        |
| WT-160                    | 1210                           |                          | 0.026     | 0.986             | 0.003         | 1.23         |
| WT-180                    | 1221                           |                          | 0.030     | 0.982             | 0.003         | 1.27         |
| WT-200                    | 1237                           |                          | 0.042     | 0.970             | 0.005         | 1.3          |

| Indices                   | Low               | Medium            | High             | Severe          |
|---------------------------|-------------------|------------------|------------------|-----------------|
| (a) Base/acid ratio:      |                   |                   |                  |                 |
| (Fe₂O₃ + CaO + MgO + Na₂O + K₂O)/(SiO₂ + Al₂O₃ + TiO₂) | <0.5               | 0.5–0.7          | 0.7–1.0         | >1.0            |
| (b) Silica percentage:    |                   |                   |                  |                 |
| (SiO₂)/(SiO₂ + Fe₂O₃ + CaO + MgO) × 100 | >50                | 50–30            | 30–5            | <5              |
| (c) Fouling index:        |                   |                   |                  |                 |
| (Fe₂O₃ + CaO + MgO + Na₂O + K₂O)/(SiO₂ + Al₂O₃ + TiO₂) × Na₂O | <0.2               | 0.2–0.5          | 0.5–1.0         | >1.0            |
| (d) Total alkali:         |                   |                   |                  |                 |
| Na₂O + K₂O               | <2.0              | 2.0–3.0           | 3.0–4.0         | >4.0            |

Figure 3. SEM and X-ray maps for major ash elements on the surface of Raw Miscanthus (RM) and WT-200.
3.3. Combustion Characterization of WT Samples

As shown in Figure 4, the combustion characteristics of the raw miscanthus (RM) and wet torrefaction (WT) samples were evaluated by a TG-DTG analysis. In the case of the TG curve, the slope peak of the weight mass reduction of the WT samples was larger than that of the RM. In the case of RM, the DTG peak of the combustion pattern can be divided into volatile matter and fixed carbon regions and appears at 200–380 and 380–500 °C, respectively. It was confirmed from WT samples that the volatile matter and fixed carbon regions moved to high temperature by wet torrefaction. In the case of the WT-160 sample, a combustion pattern of volatiles of 230–350 °C and a fixed carbon region of 350–530 °C were observed. These combustion characteristics were similar to those of WT-180 and WT-200. In particular, in the case of WT-200, it was confirmed that the combustion peaks of volatile matter and fixed carbon were sharper. Based on these results, it can be seen that the combustibility of the wet torrefaction samples improved compared to that of the raw miscanthus [28]. Figure 5 shows the results of the post-combustion analysis of RM and WT samples through TGA-FTIR. TGA is a device that measures the temperature from low to high temperature. Thus, measuring the thermal NOx, which occurs mainly at high temperature, is not easy, whereas it is easy to analyze the influence of fuel NOx [29]. As shown in Figure 5, the WT-200 shows a lower emission of NOx compared to the RM. The reason for the reduced NOx, as outlined in Table 1, is that the N value of the elemental analysis for RM is reduced by 81.25% for WT-200. The acidic solution (i.e., acetic acid et al.) converted during the wet torrefaction extracted the N component from the biomass. In addition, it was confirmed that SO2 emissions before and after treatment were similar because there was no change in the S component in the fuel itself. Similar to the TGA-DTG combustion pattern, the emissions of SO2 were measured over a range of 200–500 °C.

![Figure 4. TG-DTG curves of Raw Miscanthus (RM) and WT-samples during the combustion.](image-url)
4. Conclusions

This study analyzed upgraded fuel through product characteristics, including a comparison of biomass composition, ash composition change, combustion characteristics, and emission gas analysis to identify the characteristics of wet torrefaction fuel. Wet torrefaction pretreatment was carried out at 160, 180, and 200 °C, and both XMG and arabinan were extracted at 200 °C. In the case of WT-200, only glucan and lignin remained, indicating high levels of fixed carbon and calorific value. When comparing the RM and WT-200, the ash content decreased from 12.17 to 4.71 wt%. Among the components of the ash, in particular, it was confirmed that the content of K2O, which has a low melting point, reduced by 89.44%. From the results of the combustion characteristics obtained by TG-DTG, the volatile matter and fixed carbon region of the WT samples shifted toward a high temperature compared to RM. In the case of emission analysis post-combustion, it was found that the NOx emissions of WT-200 were reduced compared to RM as some N components in the biomass were extracted when wet torrefaction was performed. On the other hand, there was no change in SO2. Finally, wet torrefaction is a technology that complements the existing dry torrefaction, and if biomass is to be used in coal-fired power plants, it should be considered in terms of calorific value and ash. Moreover, the reduction of NOx emissions in wet torrefaction technology can be judged to be a technology that can effectively increase the use of biomass in thermal power plants. Further studies will be conducted on how to recycle or filter the acidic solution (wastewater) generated during the wet torrefaction process.
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