Changes in Moisture, Carbon, Nitrogen, Sulphur, Volatiles, and Calorific Value of Miscanthus During Torrefaction

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CHANGES IN MOISTURE, CARBON, NITROGEN, SULPHUR, VOLATILES, AND CALORIFIC VALUE OF MISCANTHUS DURING TORREFACTION

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ABSTRACT
Torrefaction tests were carried out on miscanthus samples in order to understand the changes in chemical composition at temperatures of 250–350°C and residence times of 30–120 minutes. The raw material chemical composition was moisture content 7.97%, moisture-free carbon (C) 47.73%, hydrogen (H) 5.85%, nitrogen (N) 0.28%, sulphur (S) 0.02%, volatiles (V) 83.29% for volatiles, and moisture and ash-free (MAF) calorific value (CV) 8423 BTU/lb (19.59 MJ/kg). Torrefaction at temperatures of 250°C and residence time of 30 minutes resulted in a significant decrease in moisture by about 82.68%, but the other components, C, H, N, S, and V changed only marginally. Increasing the torrefaction temperature to 350°C and residence time to 120 minutes further reduced the moisture to a final value of 0.54% (a 93.2% reduction compared to original) and also resulted in a significant decrease in the other components, C, H, N, S, and V by 58.29%, 14.28%, and 70.45%, respectively. The carbon content at 350°C and 120 minutes increased by about 4% and sulfur values were below detection limits. The calorific values increased by about 5.59% at 250°C and 30 minutes, whereas at 350°C and 120 minutes, the increase was much greater (about 75.61%) and resulted in a maximum degree of carbonization of 1.60. The H/C ratio decreased with an increase in torrefaction temperature, where a minimum value of 0.6 was observed at 350°C and 120 minutes. The regression equations developed with respect to torrefaction temperature and times have adequately described the changes in chemical composition. The surface plots developed based on the regression equations indicate that torrefaction temperatures of 300–350°C and residence times of 30–120 minutes residence time can help to increase carbon content, calorific value, and degree of carbonization to > 49.4%, >11,990 BTU/lb (27 MJ/kg), and 1.4, and reduce moisture, nitrogen, volatile, and the H/C ratio to 0.525–0.725%, 0.225–0.235%, <50 %, and <1.0.

Keywords: Miscanthus, torrefaction temperature and time, chemical composition
INTRODUCTION

Biomass is considered a carbon-neutral fuel source as it fixes atmospheric carbon by photosynthesis. The growing interest in biomass for fuel includes not only combustion to produce steam for electrical power and commercial plant duties, but also gasification to produce combustible gas (called producer gas when containing a large partial pressure of nitrogen and carbon dioxide) and syngas (principally containing carbon monoxide and hydrogen with low amounts of nitrogen and carbon dioxide). Still, the use of either producer gas or syngas in modern reciprocating or gas turbines, or to produce higher value chemicals and fuels is limited, mainly due to biomass preparation and accumulation logistics and economics. The major limitation of the raw biomass is that it contains appreciable amounts of oxygen, nitrogen, sulfur, chlorine, and fluorine, which make it thermally unstable and produces tars and oils that can be problematic in conventional equipment used for coal combustion or gasification. The relatively high O/C ratio in biomass can have advantages and disadvantages. The high oxygen content can be used to form a stoichiometric ratio of H₂ and CO to produce synthetic fuels and chemicals. Unfortunately, it is invariably necessary to “combust” (or oxidize) part of the fuel to attain the temperatures needed to thermally deconstruct the lignins and cellulose to produce H₂ and CO. Hence, it is desirable to reduce the O/C ratio in biomass prior to gasification from an exergetic point of view (Prins et al., 2006).

Biomass torrefaction has been recognized as a technically feasible method of converting raw biomass into a high energy density, hydrophobic, compactable, grindable, and lower O/C ratio solid suitable for commercial and residential combustion and gasification applications. Torrefaction is generally understood to be a thermal pre-treatment technology performed at atmospheric pressure in the absence of oxygen at temperatures between 200 and 300°C (Usla, et al., 2008). Torrefied biomass in general defines a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring in a temperature range of 200–230°C and 270–280°C (Zanzi et al. 2002). During the initial heating, drying takes place, which is followed by further heating during which more water is removed due to chemical reactions through a thermo-condensation process. This happens at over 160°C and also results in the formation of CO₂ (Zanzi et al. 2002). Between 180 and 270°C, the reaction is more exothermic, and the degradation of hemicellulose continues. At this point, the biomass begins to darken and give off moisture, carbon dioxide, and large amounts of acetic acid with some phenols that have low energy values (Zanzi et al. 2002). During the torrefaction of lignocellulosic materials, the major reactions of decomposition affect the hemicellulose. Lignin and cellulose may also decompose in the range of temperatures at which torrefaction is normally carried out, but to a lesser degree (Shafizedeh 1985 and Williams and Besler 1996). The biomass retains most of its energy and simultaneously loses its hygroscopic properties. At about 280°C, the reaction becomes entirely exothermic and gas production increases, resulting in the formation of carbon monoxide, hydrocarbons-like phenols and cresols, and other, heavier products that result from ring rupturing and scissoring organic moieties (Bourgeois and Doat 1985). There are many advantages in pretreating biomass using torrefaction before densification. Torrefaction reduces natural variability in the feedstock, which is mainly due to differences in biomass species, climatic and seasonal variations, storage conditions, and time (Lehtikangas 1999). Torrefaction helps in developing a uniform feedstock to produce high-quality densified biomass. Besides improving physical attributes, torrefaction also results in significant changes in the proximate and ultimate composition of the biomass and makes it more suitable for fuel applications. Sadaka and Negi (2009), Zanzi et al (2002) and Bridgeman et al. (2008) in their studies on torrefaction of agricultural straws and grasses indicated that the proximate and ultimate composition torrefied biomass is a strong function of temperature and residence time.

Miscanthus is classified as C4 perennial grasses, and has been identified as a potential crop for biofuels generation along with switchgrass. Studies related to the changes in chemical composition of
miscanthus samples at wide range of torrefaction temperatures are not available. The aim of the present study is to a) understand the effect of torrefaction temperature (250–350°C) and time (30–120 minutes) on chemical compositions like moisture, carbon, nitrogen, sulfur, volatiles, and calorific value and b) develop mathematical models that can help predict the changes in chemical composition.

**MATERIAL AND METHODS**

Miscanthus samples used in the present torrefaction experiments were procured from University of Illinois, Champaign, Illinois. The material was ground to a particle size of 6.35 mm size using a hammer mill. Further the ground samples were stored at about 4°C in sealed plastic containers maintained at 4°C, until tested for chemical composition.

**Chemical Composition**

ASTM standard methods (Table 1) were used for estimating the chemical composition of the raw and torrefied miscanthus samples. The chemical composition data reported in the present results are from a single measurement.

Table 1. ASTM standards for chemical composition measurement.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>ASTM Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>ASTM D3173</td>
</tr>
<tr>
<td>Carbon and Hydrogen content (%)</td>
<td>ASTM D3178</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>ASTM D3179</td>
</tr>
<tr>
<td>Volatiles (%)</td>
<td>ASTM D3175</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>ASTM D3177</td>
</tr>
<tr>
<td>Calorific value (HHV)</td>
<td>ASTM D5865</td>
</tr>
</tbody>
</table>

Table 2 shows the chemical composition of raw miscanthus samples used in this study. This data has closely matched with elemental composition analysis carried on miscanthus by Michel et al. (2006).

Table 2. Chemical composition of the raw miscanthus samples.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Chemical composition</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moisture content (%)</td>
<td>7.97</td>
</tr>
<tr>
<td>2</td>
<td>Volatiles (%)</td>
<td>83.29</td>
</tr>
<tr>
<td>3</td>
<td>Carbon content (%)</td>
<td>47.07</td>
</tr>
<tr>
<td>4</td>
<td>Hydrogen content (%)</td>
<td>5.85</td>
</tr>
<tr>
<td>5</td>
<td>Nitrogen content (%)</td>
<td>0.28</td>
</tr>
<tr>
<td>6</td>
<td>Sulfur content (%)</td>
<td>0.02</td>
</tr>
<tr>
<td>7</td>
<td>Calorific value (MAF)</td>
<td>8038 (BTU/lb) or (18.69 MJ/kg)</td>
</tr>
</tbody>
</table>

Note:
1) Carbon, hydrogen, nitrogen, sulfur, and calorific value are reported on a moisture-free basis and calorific value on a moisture and ash free basis.
2) Conversion from BTU/lb to MJ/kg: Multiply BTU/lb by 0.002326

**Torrefaction Process Design**

An industrial fluidized bed bath (Techne Inc, NJ, USA) with a temperature range of 50-600°C was used as a bubbling sand bed reactor in the present torrefaction experiments. The reactor was instrumented to record the oxidizer temperature which was used for burning the off-gases produced during torrefaction. The schematic of the torrefaction system is shown in Figure 1.
Figure 1. Schematic of the Biomass Torrefaction Unit.

The current process includes heating the sand bed to a constant temperature and maintaining an inert environment using N₂. Once the system was stabilized in terms of temperature and gas flow, a known quantity of the biomass was placed in an iron mesh container and manually pushed into the sand bed. The material was left in the bubbling sand bed for the desired residence time after which the iron mesh container was pulled out and cooled with a nitrogen purge to speed up the cooling process. The cooled samples were further packed under a vacuum in moisture proof bags for further testing. An electrically heated thermal oxidizer was placed in line with the torrefaction system to burn out volatiles before they are released into the environment. The composition of the volatiles was not analyzed in the present studies.

**Experimental Procedure**

100 g of ground miscanthus samples of 6 mm in size were placed in the iron mesh container. Once the chamber reaches the desired temperature and remains stable, the iron mesh container was manually pushed into the sand bed. The inert environment was maintained using N₂. The recommended N₂ flow rates of 1.8–2.2 SCFM (standard cubic feet per minute) were maintained as recommended by the manufacturer.

In the present study at high torrefaction temperature the bed material (aluminum oxide) exhibited static charge and was getting attached to the torrefied biomass. To overcome this limitation torrefied biomass was initially sieved in a Ro-Tap sieve shaker using No: 50 (0.0117 inches) and was also further sieved using 250-μm (No: 60) before the chemical analysis. The sieving procedure followed has reduced the influence of bed medium on the chemical composition studied.

**Experimental Plan**

Torrefaction was carried out at three different temperatures (250, 300, and 350°C) and at three different residence times (30, 60, and 120 minutes). At each temperature under study, the experiments were conducted at three residence times.
Data Analysis

The data analysis has been carried out with the following objectives:

- Comparing the changes in the chemical composition at various torrefaction temperatures and times with respect to the original values
- Developing regression models in terms of torrefaction temperature and times to predict chemical composition.
- Developing response surface models to understand the interactive effect of torrefaction temperatures and times on the chemical composition.

The general form of the regression and response surface model is given in Equation 1 (Montgomery 1976)
\[ y = f(x_1, x_2, x_3, \ldots, x_n) + \varepsilon \]  

where \( y \) is the response or dependent variable, \( x_1, x_2, x_3, \ldots, x_n \) are the process or independent variables; and \( \varepsilon \) is the noise or error observed in the response variable ‘y’.

In the present study, response surface plots were developed using the regressions equations developed for the torrefaction temperature and time with respect to the response variables which includes moisture (%), carbon (%), hydrogen (%), nitrogen (%), volatile (%), calorific value (HHV, BTU/lb), degree of carbonization, and H/C ratio. These plots were further used to understand the interactive effects of the process variables on the chemical composition of torrefied miscanthus.

RESULTS

Regression Models

Equations 2–9 are the regression models developed for the chemical composition of miscanthus with respect to the torrefaction temperature \( (x_1) \) and time \( (x_2) \):

- **Moisture Content (%)** = \[ 3.40 - 0.0077x_1 - 0.0079x_2 + 0.000013x_1x_2 \]  
  \( (r^2 = 0.84) \)  
  \( \ldots (2) \)

- **Carbon Content (%)** = \[ 48.30 - 0.0016x_1 - 0.022x_2 + 0.000107x_1x_2 \]  
  \( (r^2 = 0.98) \)  
  \( \ldots (3) \)

- **Hydrogen Content (%)** = \[ 13.71 - 0.030x_1 - 0.00024x_2 - 0.000003x_1x_2 \]  
  \( (r^2 = 0.84) \)  
  \( \ldots (4) \)

- **Nitrogen Content (%)** = \[ 0.284 - 0.000042x_1 + 0.00030x_2 - 0.000002x_1x_2 \]  
  \( (r^2 = 0.96) \)  
  \( \ldots (5) \)

- **Volatile content (%)** = \[ 228.74 - 0.55x_1 - 0.023x_2 - 0.000086x_1x_2 \]  
  \( (r^2 = 0.82) \)  
  \( \ldots (6) \)

- **Calorific Value (MA, BTU / lb)** = \[ 1433 + 24.89x_1 + 50.88x_2 - 0.120x_1x_2 + 0.065x_2^2 \]  
  \( (r^2 = 0.86) \)  
  \( \ldots (7) \)

- **H / C ratio** = \[ 3.089 - 0.0058x_1 - 0.0014x_2 - 0.000008x_1x_2 \]  
  \( (r^2 = 0.92) \)  
  \( \ldots (8) \)

- **DC** = \[ 0.17 + 0.0029x_1 + 0.0060x_2 - 0.000014x_1x_2 \]  
  \( (r^2 = 0.85) \)  
  \( \ldots (9) \)

As seen above the regressions equations developed for chemical composition has adequately described the process with a lowest correlation coefficient value of 0.82 for volatile content and highest of 0.98 for carbon. The observed and predicted values also indicated that equations have predicted very closely. All the models developed were statistically significant at P<0.001.
Figure 2 indicates that the moisture content is greatly influenced by torrefaction temperature and time. A final moisture content of about 0.6% was reached at 350°C and 120 minutes. Significant decrease in moisture content of about 82.68% was observed at 250°C and 30 minutes. Increasing the temperature to 300 and 350°C has decreased the moisture content by about 85.82 and 92.47% respectively. Increase in residence times to 60 and 120 minutes resulted in similar changes in the moisture content. It is very clear from the above plot that maximum moisture is removed at 250°C and 30 minutes. The surface plot (Figure 3) drawn based on the regression equation (Equation 2) indicates...
that the lowest moisture of about 0.6 was achievable at a temperature range of 320–350°C at 30 minutes residence time.

**Carbon Content (%)**

![Graph showing carbon content of torrefied miscanthus samples.](image)

Figure 4. Carbon content of torrefied miscanthus samples.

The influence of torrefaction temperature and time on the carbon content of the miscanthus samples is shown in Figure 4. Carbon content increased from was 1.40–2.15% with an increase in
temperature from 250 to 350°C at 30 minutes of residence time. At 350°C, further increasing the residence time to 120 minutes increased the carbon content to about 5.45%. Figure 5 clearly indicates that carbon content >49.6% was obtained at temperature >320°C and residence time >100 minutes.

Hydrogen Content (%)

![Graph showing hydrogen content of miscanthus samples.]

**Figure 6.** Hydrogen content of miscanthus samples.

![Graph showing the effect of torrefaction on hydrogen content.]

**Figure 7.** Effect of torrefaction on hydrogen content.
The change in the hydrogen content of the miscanthus samples at different torrefaction temperatures and times is shown in figure 6. Hydrogen content decrease at torrefaction temperatures and time of 250, 300, and 350°C and 30 minutes were 1.70, 5.98 and 54.70. The decrease was very significant at the higher temperature of 350°C. Similar results were realized at 60 and 120 min residence times. The surface plot (Figure 7) shows the relationship for hydrogen content as a function torrefaction temperature and time. A minimum hydrogen content value of 2.44 was observed at a torrefaction temperature of 350°C and 120 minutes.

Nitrogen Content (%)

**Figure 8.** Nitrogen content of torrefied miscanthus samples.

The effect of torrefaction temperature and time on nitrogen content is shown in figures 8 and 9. The decrease in nitrogen content at 250, 300, and 350°C and 30 minutes was 3.57, 7.14, and 10.71%. The surface plot (Figure 9) show that the decrease in nitrogen content was gradual up to 280°C, but thereafter the decrease became very steep.
Figure 9. Effect of torrefaction on nitrogen content.

The change in the volatile content of the material was marginal (less than 0.5%) at 250 and 300°C for a 30 minutes residence time. Further increasing the temperature and residence time to 350°C and 120 minutes reduced the volatile content significantly. The decrease at 350°C for 60 minutes was 70.45%. The surface plot (Figure 11) shows that the volatiles are reduced over 50% at temperatures >320°C at all residence times (>30 min).

Figure 10. Volatile content of the torrefied miscanthus samples.
Figure 11. Effect of torrefaction on volatile content.

Increasing the temperature from 250, 300, and 350°C for 120 minutes residence time significantly increased the heating value (HV) on moisture and ash free basis from an initial value of 8038 to 11812, 12822, and 13561 BTU/lb (18.69, 27.47, 29.82 and 31.54 MJ/kg). The surface plot
(Figure 13) indicates that both the torrefaction time and temperature are having an equal effect on the calorific value. Temperatures >320°C and times >60 minutes, the calorific value has increased to >10,000 BTU/lb (>23.26 MJ/kg).

**Figure 13.** Effect of torrefaction on calorific value (MAF, BTU/lb).

**H/C Ratio**

H/C ratio did not decrease significantly at lowest residence time and temperature. The percent decrease at 250 and 300°C for 30 minutes was about 3.65–4.44%, whereas at 120 minutes the decrease was about was 32.94%. The surface plot has indicated that H/C ratios of less than one are achievable at torrefaction temperatures >300°C and residence times of >40 minutes. The H/C value dropped to 0.6 at temperatures >320°C and residence time of >90 minutes.

**Figure 14.** H/C ratio of torrefied miscanthus samples.
**Figure 15.** Effect of torrefaction on the H/C ratio.

**Figure 16.** Degree of carbonization of miscanthus sample.
The degree of carbonization (DC) is the ratio of the calorific value of torrefied biomass to raw biomass. Torrefaction temperature had a significant effect on DC values. The increase in DC was more significant at a higher temperature of 350°C and at residence times >30 minutes (Figure 16). The surface plot drawn (Figure 17) indicated that temperatures of about 320°C and residence times >90 minutes has resulted in DC values greater than 1.4. A summary of the response surface plots is tabulated in Table 3.

**Figure 17.** Effect of torrefaction on the degree of carbonization.

**Table 3.** Summary of response surface plots on the chemical composition of miscanthus.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Torrefaction temperature (°C)</th>
<th>Torrefaction time (min)</th>
<th>Range</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>250</td>
<td>30–120</td>
<td>&gt;1.025</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>250–300</td>
<td>30–120</td>
<td>0.725–1.025</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>300–350</td>
<td>30–120</td>
<td>0.525–0.725</td>
<td>Minimum</td>
</tr>
<tr>
<td>Carbon content (%)</td>
<td>320–350</td>
<td>90–120</td>
<td>&gt;49.4</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>270–350</td>
<td>60–120</td>
<td>48.6–49.4</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>250–350</td>
<td>30–120</td>
<td>47.8–48.6</td>
<td>Minimum</td>
</tr>
<tr>
<td>Hydrogen content (%)</td>
<td>250–280</td>
<td>30–120</td>
<td>&gt;4.9</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>280–300</td>
<td>30–120</td>
<td>3.9–4.9</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>300–350</td>
<td>30–120</td>
<td>2.9–3.9</td>
<td>Minimum</td>
</tr>
<tr>
<td>Nitrogen content (%)</td>
<td>250–300</td>
<td>30–120</td>
<td>&gt;0.245</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>300–320</td>
<td>30–120</td>
<td>0.235–0.245</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>320–350</td>
<td>30–120</td>
<td>0.225–0.235</td>
<td>Minimum</td>
</tr>
</tbody>
</table>
### Table 4: Summary of Char Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range (°C)</th>
<th>Residence Time</th>
<th>Units</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volatile content (%)</strong></td>
<td>250–280</td>
<td>30–120</td>
<td>&gt;80</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>280–300</td>
<td>30–120</td>
<td>50–80</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>300–350</td>
<td>30–120</td>
<td>30–50</td>
<td>Minimum</td>
</tr>
<tr>
<td><strong>Calorific value</strong></td>
<td>300–350</td>
<td>80–120</td>
<td>&gt;11,900</td>
<td>Maximum</td>
</tr>
<tr>
<td><em>(HHV, BTU/lb)</em></td>
<td>250–350</td>
<td>50–120</td>
<td>10,400–11,900</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>250–350</td>
<td>30–90</td>
<td>8,400–10,400</td>
<td>Minimum</td>
</tr>
<tr>
<td><strong>Degree of carbonization</strong></td>
<td>320–350</td>
<td>80–120</td>
<td>&gt;1.4</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>300–350</td>
<td>60–120</td>
<td>1.2–1.4</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>250–300</td>
<td>30–60</td>
<td>1.0–1.2</td>
<td>Minimum</td>
</tr>
<tr>
<td><strong>H/C ratio</strong></td>
<td>250–280</td>
<td>30–120</td>
<td>&gt;1.4</td>
<td>Maximum</td>
</tr>
<tr>
<td></td>
<td>260–300</td>
<td>30–120</td>
<td>1.0–1.4</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>300–350</td>
<td>30–120</td>
<td>&lt;1.4</td>
<td>Minimum</td>
</tr>
</tbody>
</table>

From the summary of the bar and surface plots, it is very clear that high temperature (>300°C) and residence times (>30 minutes) are required to minimize the moisture content, hydrogen, nitrogen volatile, and H/C ratio while maximizing carbon content, calorific value, and degree of carbonization. These results are highlighted in Table 4. The trends regarding changes in chemical composition agree with the experimental findings of Sadaka and Negi, 2009, Zanzi et al. 2002 and Bridgeman et al. 2008.

Bridgeman et al. (2008) in their study of reed canary grass and wheat straw torrefaction at 230, 250, 270, and 290°C for 30 minute residence times, found that the moisture content decreased from an initial value of 4.7% to 0.8%, which matches with the present results where a moisture content in the range of 0.525–0.725% was obtained in the torrefaction temperature and residence times in the range of 250–300°C and 30–120 minutes. The present results of calorific value at 250–300°C and 30–90 minutes, which was in the range of 8,400–10,400 BTU/lb has matched with their findings for reed canary grass and wheat straw at 290°C and 30 minutes (9372 and 9716 BTU/lb).

Zanzi et al. (2002) in their study on the torrefaction of miscanthus has made similar observations where increasing the torrefaction temperature and residence time has increased the carbon content and decreased the hydrogen and nitrogen content. In their studies at 280°C for 180 minutes, the carbon content increased to about 52% from the initial value of 43.5% while the hydrogen and nitrogen content decreased from 6.49 to 5.54% and from 0.90 to 0.65%. The maximum carbon content was about 2% lower compared to their studies, which can be due to the higher residence time of 180 minutes used in their studies. The nitrogen content which is about 0.9% in their studies has reduced to 0.25% and this value has reduced by about 3.57, 7.14, and 10.71% at 250, 300 and 350°C for 30 minutes of residence time. These values are less compared to the Zanzi et al (2002) observation, where they have reported about 27% reduction at 290°C for 30 minutes.

Sadaka and Negi (2009) in their studies on the torrefaction of wheat, rice straws, and cotton gin waste at 200, 260 and 315°C and 60, 120 and 180 minutes observed a significant loss of moisture, about 70.5%, 49.4% and 48.6%. The loss of moisture of about 85.82% in the present study matches with the wheat straw. They have also reported that the calorific value has increased by about 6–15%, which matches with the present values, about 5–10% at torrefaction temperatures and times of 250–300°C and 30–60 minutes.

**DISCUSSION**

In this study, moisture loss during torrefaction was significant at all torrefaction temperatures and residence times. This loss can be attributed to devolatilization and carbonization of hemicellulose
and cellulose which typically happens at higher temperatures (>250°C) and longer residence times (>30 minutes). Bergman and Kiel (2005) and Prins (2005) in their studies have reported that drying and depolymerization occurs between 225 and 325°C for hemicelluloses. The loss of moisture during torrefaction can be due two different mechanisms: a) moisture evaporation, and b) dehydration reactions between organic molecules (Bridgeman et al. 2008). Along with the moisture, there are other organic and inorganic products released, which is indicated by volatile content loss during this torrefaction study (Figures 10 and 11).

Increase in torrefaction temperature in general results in an increase in carbon content and simultaneously decreases the hydrogen and oxygen content due to the formation of water, carbon monoxide, and carbon dioxide. In this study there is a significant increase in carbon content and decrease in hydrogen content of the torrefied miscanthus samples with increase in torrefaction temperature and time. This results in a decrease in H/C and O/C ratio, resulting in the formation of less smoke and less water vapor formation and also less energy loss during combustion and gasification processes. Lower torrefaction process conditions like 250 and 300°C and a 30 minute residence time showed only marginal changes in the hydrogen content of the samples. However, as the temperature increases to greater than 300°C, the reduction of hydrogen content increased significantly, which might be due to the formation of hydrocarbons such as CH₄ and C₂H₆. In addition, the sulfur content of the samples was well below the detection limits at higher torrefaction temperatures (>300°C), which has matched with the findings of Mani et al. (2008) studies on torrefaction of forest residues.

The heating value or the calorific value of biomass is an important characteristic that determines its value in energy applications (Arias et al., 2008). The calorific value of the torrefied miscanthus samples have increased with an increase in temperature and time, where higher temperatures have resulted in higher calorific values. This increase in calorific value can be correlated to the loss of volatiles (Figures 10 and 11), where there is a significant decrease in volatile content at high torrefaction temperatures and times. The increase in the heating value or calorific value is due to a decrease in the moisture content and an increase in the carbon content of the samples, as reported by Zanzi et al. (2002) and Nimlos et al. (2003). According Bergman and Kiel (2005) and Bridgeman et al. (2008) the loss of volatiles during the torrefaction process can result in an increase in the energy density of the biomass. The effect was similar on the degree of carbonization or energy densification value (which is the ratio of torrefied calorific value to raw biomass calorific value).

**CONCLUSIONS**

The following conclusions are drawn from the present research:

1. Increasing the torrefaction temperature (>280°C) and time (>30 minutes) significantly decreased the moisture content, hydrogen content, and H/C ratio, which might be due to devolatilization of hemicellulose and cellulose.

2. Increasing the torrefaction temperature (>300°C) and time (30 minutes) increased the carbon content and decreased the hydrogen content, which can be due to the formation of water, carbon monoxide, and carbon dioxide.

3. The calorific value measured increased with increasing torrefaction temperature and time, which might be due to the loss of volatiles. This effect was more significant at temperatures greater than 300°C.

4. The regression models developed in terms of torrefaction temperature and time with respect to chemical composition has correlation coefficient values from 0.82 for volatile content to 0.98 for carbon content.

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REFERENCES

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