

Article

Some Chemical Compositional Changes in Miscanthus and White Oak Sawdust Samples during Torrefaction

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Received: 13 July 2012; in revised form: 14 September 2012 / Accepted: 19 September 2012 /

Published: 16 October 2012

Abstract: Torrefaction tests on miscanthus and white oak sawdust were conducted in a bubbling sand bed reactor to see the effect of temperature and residence time on the chemical composition. Process conditions for miscanthus and white oak sawdust were 250–350 °C for 30–120 min and 220–270 °C for 30 min, respectively. Torrefaction of miscanthus at 250 °C and a residence time of 30 min resulted in a significant decrease in moisture—about 82.68%—but the other components—hydrogen, nitrogen, sulfur, and volatiles—changed only marginally. Increasing torrefaction temperatures to 350 °C with a residence time of 120 min further reduced the moisture content to 0.54%, with a significant decrease in the hydrogen, nitrogen, and volatiles by 58.29%, 14.28%, and 70.45%, respectively. Regression equations developed for the moisture, hydrogen, nitrogen, and volatile content of the samples with respect to torrefaction temperature and time have adequately described the changes in chemical composition based on R^2 values of >0.82 . Surface plots based on the regression equation indicate that torrefaction temperatures of 280–350 °C with residence times of 30–120 min can help reduce moisture, nitrogen, and volatile content from 1.13% to 0.6%, 0.27% to 0.23%, and 79% to 23%, with respect to initial values. Trends of chemical compositional changes in white oak sawdust are similar to miscanthus. Torrefaction temperatures of 270 °C and a 30 min residence time reduced the moisture, volatiles, hydrogen, and nitrogen content by about 79%, 17.88%, 20%, and 5.88%, respectively, whereas the carbon content increased by about 3.5%.

Keywords: miscanthus; white oak sawdust; torrefaction; temperature; time; chemical composition

1. Introduction

According to Cherubini *et al.* [1], carbon dioxide (CO₂) emissions from biomass combustion are considered climate neutral if the bioenergy system is carbon (C) flux neutral, where the CO₂ released from biofuel combustion equals the amount of CO₂ sequestered in the biomass. Not all biofuels made from different feedstock materials have the same impact, as some may include large inputs of nitrate ion (NO₃), which has a direct correlation to their carbon footprint and can result in negative energy balances. According to Pimentel and Patzek [2], Sheehan *et al.* [3], and Shapouri *et al.* [4], the net energy gain varies based on the type of feedstock material used.

Energy from biomass can be produced from different thermochemical (combustion, gasification, and pyrolysis), biological (anaerobic digestion and fermentation), or chemical (esterification) processes, where direct combustion can provide a near-term energy solution [5–8]. The use of biomass for fuels applications on a commercial scale is limited, mainly due to biomass preparation, accumulation logistics, and economics [9,10]. The major limitation of 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 [11]. In their studies on formulation, pretreatment, and densification options for cofiring higher percentages with coal, Tumuluru *et al.* [12] identified that significant differences exist in the chemical compositions of biomass to coal; biomass has higher fractions of hydrogen, oxygen, and volatiles content, as well as lower carbon fractions and calorific value as compared to coal. These differences affect the combustion properties and limit the percentage of biomass that can be co-fired with coal. Chlorine in the biomass can have a detrimental impact on the boiler tube and can contribute to the corrosion of the boiler surface, depending on the concentration [12]. Certain biomass fuels, however, may contain relatively high amounts of chlorine or fluorine. During combustion, chlorine is released as HCl and fluorine as HF. Both HCl and HF are highly corrosive and can destroy boiler surfaces [13]. Studies on the effect of biomass fluorine with regard to combustion behavior and off-gas emissions are scarce.

1.1. Biomass Challenges

Biomass sources have a number of quality and logistical challenges in common. Inconsistent moisture is one of those primary challenges. Moisture in biomass feedstocks needs to be adjusted to suit the conversion process. Uncontrolled variations in moisture reduce the efficiency of the process and increase costs [14]. Also, high moisture in the biomass leads to natural decomposition, resulting in loss of quality and storage issues, such as off-gas emissions. One major limitation of biomass is its low energy and bulk density as compared to conventional fossil fuels. This results in varied biomass performance for different end-use applications, as well as increasing transportation and handling costs. In addition, biomass has irregular shapes and contains a large amount of oxygen relative to carbon and

hydrogen. These biomass properties result in many problems, such as high particle-size reduction energies, high transportation costs, feeding problems due to poor flowability, and lower heat and mass-transfer rates during thermochemical conversion processes (*i.e.*, gasification and pyrolysis). Issues related to ash become increasingly important when biomass is considered for combustion along with coal. Straw and other herbaceous fuels like miscanthus or grass have a higher content of ash than wood because they uptake more nutrients during growth. In the case of wood fuels, the bark content in the fuel has an influence on the ash content as bark has a higher ash content as well as higher levels of mineral impurities, such as sand and soil [15–17]. The concentrations of inorganic elements in biomass—including silica, sulfur, and alkali metals—are an important specification because they form alkali silicates or sulfates that melt or soften at temperatures as low as 700 °C [18].

To overcome many of these challenges, biomass needs to be preprocessed before being converted into other products. Raw biomass can rarely be used in the conversion process without some form of preprocessing. Grinding is a commonly used preprocessing operation that helps achieve a consistent particle size. However, the performance of many grinders is limited by the moisture content of the biomass [14]. High moisture content results in materials with inconsistent particle sizes that may not react consistently during the conversion processes, thereby reducing the efficiency of the process. In addition, the collection and transport efficiencies of biomass are low, as the material is typically loaded and unloaded in batches [14]. Raw biomass that is thermally unstable when used in a thermochemical conversion process such as gasification can lead to the formation of condensable tars and result in problems like gas-line blockage [10]. Preprocessing the biomass to improve its performance in either thermochemical or biochemical conversion processes is a good option. Common pretreatment methods include chemical, mechanical, and thermal-like acid pretreatment, or the ammonia fiber explosion method (AFEX), steam explosion, and torrefaction. Most of these pretreatment methods help break the amorphous and crystalline regions of the biomass and make the material more amenable to bio- or thermo-chemical conversions.

1.2. Torrefaction

Biomass torrefaction has been recognized as a technically feasible method of converting raw biomass into a high-energy density, hydrophobic, compactable, grindable, and low O/C ratio solid suitable for commercial and residential combustion and gasification applications. Torrefaction is generally understood to be a thermal pretreatment technology where a group of products are formed from the partially controlled and isothermal pyrolysis of biomass occurring in the absence of oxygen at temperatures between 200 and 300 °C [19,20]. Initial stages of torrefaction involve basic drying where only the surface moisture is removed; further drying results in the removal of moisture and other volatiles due to chemical reactions through the thermo-condensation process, which typically happens at temperatures above 160 °C. At this temperature, not only moisture and some volatiles but also some CO₂ gets released [20]. At 180 and 270 °C temperatures, the reaction is mostly exothermic, which results in hemicellulose degradation. At this point, the biomass begins to darken and give off additional moisture, carbon dioxide, and large amounts of acetic acid with some phenols that have low energy values [20]. At temperatures ≥ 280 °C, the biochemical reactions become completely exothermic, resulting in the production of CO, CO₂, and CH₄ gases, in addition to hydrocarbons like phenols,

cresols, and other heavier products due to ring rupturing and scissoring of organic moieties [21]. During torrefaction of lignocellulosic materials in particular, the major reactions of decomposition affect the hemicellulose, whereas lignin and cellulose decompose to a lesser extent [22,23]. Hemi-cellulose degradation results in the loss of volatiles, which have low energy content, and most of the energy content of the biomass material is retained. Hemicellulose degradation also results in the loss of OH groups, making biomass material hydrophobic. According to Shafizadeh [22] and Williams and Besler [23], the major reactions of decomposition affect the hemicelluloses, whereas lignin and cellulose decompose to a lesser degree. Bourgois and Doat [21] recommend not torrefying biomass above 300 °C, as it leads to extensive devolatilization and initiates pyrolysis.

Other advantages in pretreating biomass using torrefaction include: (a) a reduction in the feedstock natural variability, mainly due to differences in the biomass species resulting in different chemical compositions, climatic and seasonal variations, storage conditions, and time, which helps develop a uniform feedstock for bioenergy applications; (b) an improvement in physical attributes like reduced moisture content, better grindability, particle size, and sphericity; and (c) a reduction in oxygen and hydrogen content, which increases the percentage of carbon content, making the biomass more suitable as a fuel. In addition, many researchers have investigated the effect of torrefaction process time and temperature on the physical and chemical composition [19–21,24–30].

Recent studies by Tumuluru *et al.* [9,12] on pretreatment methods for bioenergy applications, such as torrefaction, indicated that torrefied material makes a good fuel for biofuels applications, such as co-firing. In addition, it has been noted that torrefaction of biomass not only increases biomass energy properties, but produces some higher hydrocarbons as well, which can typically be used for producing chemicals or for improving overall energy efficiency [31]. Some recent experimental and techno-economical studies on torrefaction include: (a) the effects of particle size, different corn stover components, and gas residence times on the torrefaction of corn stover by Medic *et al.* [32]; (b) the techno-economic analysis of a production-scale torrefaction system for cellulosic biomass upgrading by Shah *et al.* [33]; (c) biomass upgrading by torrefaction for the production of biofuels by van der Stelt *et al.* [34]; (d) the study of particle size effect on biomass torrefaction and densification by Peng *et al.* [35]; (e) recent advances in biomass pretreatment, torrefaction fundamentals, and technology by Chew and Doshi [36]; and (f) studies by Tumuluru *et al.* [37] on the response surface analysis of elemental composition and energy properties of corn stover during torrefaction. In general, response surface methodology (RSM) is the commonly used method to understand the effect of process variables on the product properties. RSM is a combination of mathematical and statistical techniques and is widely used to study process and product development data [38–40].

Miscanthus (*Miscanthus x giganteus*) is classified as a C₄ perennial grass and is a potential crop for bioenergy production, along with switchgrass. White oak wood is widely used by the furniture and housing industries. White oak sawdust is a byproduct available from the lumber industry and is a good bioenergy application source. Different types of torrefaction reactors (*i.e.*, screw auger, fixed and fluidized bed, and bubbling sand bed) are generally used to carry out torrefaction studies. Of these, the fixed and fluidized bed reactors are most commonly used in laboratory-scale studies. No literature is available on chemical compositional changes in white oak sawdust samples during torrefaction in a bubbling sand bed reactor.

The aim of this present study is to understand the effect of torrefaction temperature and time on some chemical compositions of miscanthus and white oak sawdust samples. Specific objectives include: (a) torrefaction of miscanthus in the temperature range of 250–350 °C at 30–120 min to understand the changes in moisture, carbon, hydrogen, nitrogen, and volatiles content; and (b) developing response surface models for miscanthus data that can help predict the changes in chemical composition due to torrefaction. In the case of white oak sawdust samples, only two temperatures and one residence time (230 and 270 °C and 30 min) were selected, as our studies on corn stover [37] and miscanthus indicated a significant weight loss when biomass is torrefied at temperatures greater than 300 °C and residence times of >30 min.

2. Material and Methods

Miscanthus (*Miscanthus x giganteus*) samples used in the present torrefaction experiments were procured from the University of Illinois in Champaign, IL, USA. The material was ground to a particle size of 6.35 mm using a hammer mill. The ground samples were further stored at about 4 °C in sealed plastic containers until being tested for chemical composition. White oak sawdust samples were procured from the local lumber industry and were further sieved to have a consistent 2-mm particle size.

2.1. Chemical Composition

ASTM standard methods (see Table 1) were used to estimate the chemical composition of raw and torrefied miscanthus samples. Table 2 indicates the chemical composition of the raw miscanthus and white oak saw dust samples. This proximate data of the raw miscanthus samples reported in Table 2 has closely matched with the values reported by Michel *et al.* [41]. The chemical composition data of raw and torrefied miscanthus and white oak saw dust samples reported in the present work are from a single measurement.

Table 1. ASTM standards for chemical composition measurement.

Chemical Composition (%)	ASTM Standard
Moisture content	ASTM D3173
Carbon and hydrogen content	ASTM D3178
Nitrogen	ASTM D3179
Volatiles	ASTM D3175
H/C: Number of hydrogen atoms/number of Carbon atoms = (%H/1)/(%C/12)	

Table 2. Chemical composition of the raw miscanthus and white wood oak sawdust samples.

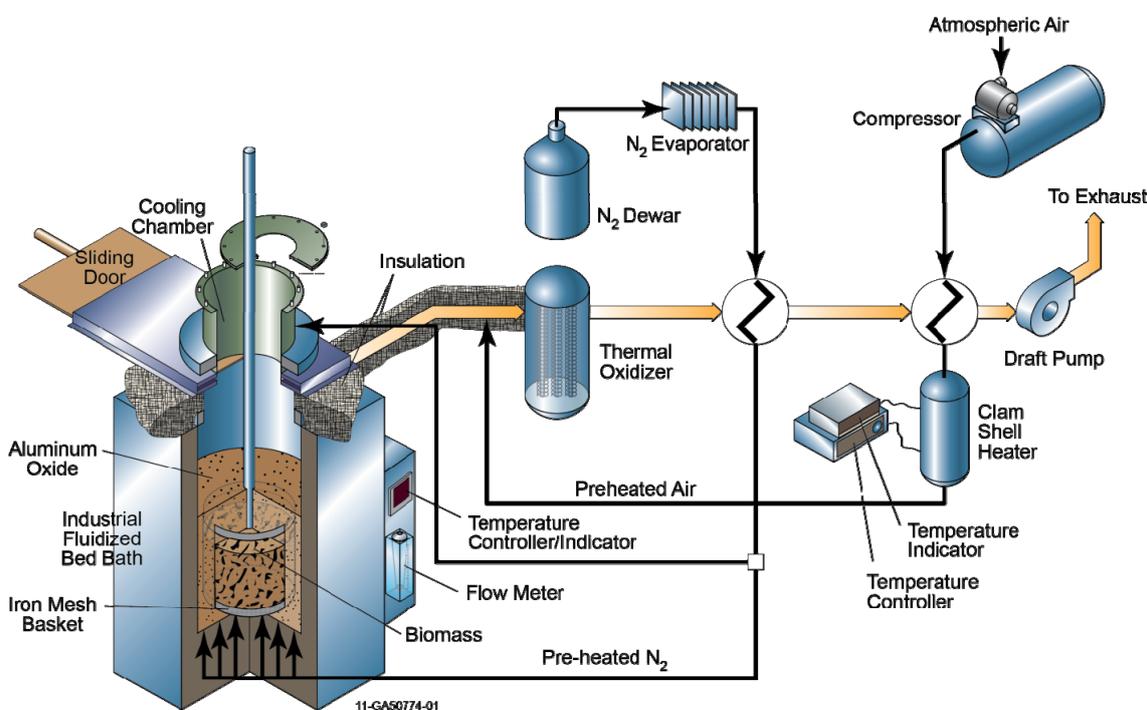
S. No	Chemical composition	Miscanthus	White oak sawdust
1	Moisture content (%)	7.97	8.53
2	Volatiles (%)	83.29	80.75
3	Carbon content (%)	43.45	50.28
4	Hydrogen content (%)	5.85	5.91
5	Nitrogen content (%)	0.28	0.17

Note: Carbon, hydrogen, nitrogen, sulfur, and volatiles are reported on a moisture-free basis.

2.2. Torrefaction Process Design

Industrial fluidized bed bath (Techne Inc., NJ, USA) with a temperature range of 50–600 °C was used as a bubbling sand bed reactor for the torrefaction experiments. The unit includes a test chamber that holds the sand bed (aluminum oxide in the present study) and an iron mesh basket to contain the sample material. A gas line connects to the test chamber, delivering a flow of nitrogen gas to maintain the necessary inert environment. An electrically heated thermal oxidizer is placed in line with the torrefaction system to burn out volatiles before they are released into the environment. The reactor is instrumented to record both bed and oxidizer temperatures used to burn the off gases produced during torrefaction based on U.S. Environmental Protection Agency (EPA) regulations [37]. A schematic of the torrefaction system is shown in Figure 1.

Figure 1. Bubbling sand bed biomass torrefaction unit (Image courtesy of *Journal of Biobased Materials and Bioenergy*) [37].



2.3. Experimental Procedure

Torrefaction process includes heating the sand bed at a constant temperature and maintaining inert environment in the reactor using nitrogen. The N₂ flow rates of 1.8–2.2 standard cubic feet per minute (SCFM) were used in these tests. Once the system temperature and gas flow rates were stabilized, a 100-g biomass sample is placed in the iron mesh container and manually pushed into the sand bed. The sample is further left in the sand bed for the desired residence time, after which the iron mesh container is pulled out and cooled. These cooled samples were further packed under a vacuum in moisture-proof bags for future testing [37]. As the bed medium got attached with the torrefied biomass, the torrefied biomass was sieved before packing. In the present study we have not analyzed the volatiles produced during the torrefaction process. The complete details of operation of the bubbling sand bed torrefier are described by Tumuluru *et al.* [37].

The torrefaction tests were carried out at three different temperatures (*i.e.*, 250, 300, and 350 °C) and residence times (*i.e.*, 30, 60, and 120 min) for miscanthus, and at two different temperatures (*i.e.*, 220 and 270 °C) and one residence time (*i.e.*, 30 min) for white oak sawdust (see Table 3). Each torrefaction experiment was conducted a single time. During our experimental studies, it was observed that at torrefaction temperatures of 250 °C, the bubbling sand medium (aluminum oxide) had adhered to the biomass surface. This limitation was overcome by sieving the torrefied biomass using a Ro-Tap sieve shaker using No. 50 and No. 60 screens to reduce the bed medium influence on the chemical composition. Further, the sieved torrefied biomass was used for chemical analysis. The torrefaction experiments were carried out one time.

2.4. Response Surface Analysis

For the miscanthus torrefaction data presented in Table 3, response surface models were developed for torrefaction process variables like torrefaction temperature (°C) and torrefaction time for chemical compositions studied. Equation (1) indicates the form of the second order polynomial used in the present study [42]:

$$y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^n \sum_{j=1}^n b_{ij} x_i x_j + \varepsilon \quad (1)$$

where y is the dependent variable (observed), x_i and x_j are the coded independent variables, b_0 b_i b_j are coefficients, n is the number of independent variables, and ε is a random error. Response surface plots were drawn using the response surface models developed. An analysis of variance test was carried out to understand whether temperature and time had a statistically significant effect on the different chemical composition studied. Statistica (data analysis software system) version 9.1 (StatSoft, Inc., Tulsa, OK, USA) was used for the present data analysis.

Table 3. Experimental design followed for torrefaction studies.

Miscanthus	Torrefaction Process Conditions	
	Torrefaction Temperature (°C)	Torrefaction Time (min)
1	250	30
2	250	60
3	250	120
4	300	30
5	300	60
6	300	120
7	350	30
8	350	60
9	350	120
White Oak Sawdust		
1	230	30
2	270	30

3. Results

3.1. Miscanthus Experimental Data

The data obtained on miscanthus torrefaction at three levels of temperature (*i.e.*, 250, 300, and 350 °C) and three levels of residence time (*i.e.*, 30, 60, and 120 min) were used to develop the bar plots and response surface models. Furthermore, these response surface models were used to draw the three-dimensional surface plots to understand the interactive effects of the process variables on the chemical compositions studied.

3.2. Regression Equations

Equations (2)–(6) are the regression models developed for the chemical composition of miscanthus with respect to torrefaction temperature (x_1) and time (x_2), in the range of 250–350 °C and 30–120 min:

Moisture content

$$= 3.51 - 0.004x_1 - 0.031x_2 - 0.000010x_1^2 + 0.000073x_2^2 + 0.000055x_1x_2 \quad (R^2 = 0.97) \quad (2)$$

Carbon content

$$= 52.54 - 0.0089x_1 - 0.214x_2 - 0.00001x_1^2 + 0.00051x_2^2 + 0.00060x_1x_2 \quad (R^2 = 0.96) \quad (3)$$

Hydrogen content

$$= -34.26 + 0.295x_1 + 0.0053x_2 - 0.0005x_1^2 - 0.00004x_2^2 - 0.000003x_1x_2 \quad (R^2 = 0.99) \quad (4)$$

Volatile content

$$= -667.29 + 5.577x_1 - 0.139x_2 - 0.010x_1^2 + 0.001x_2^2 - 0.00008x_1x_2 \quad (R^2 = 0.99) \quad (5)$$

$$\frac{H}{C} \text{ ratio} = -6.477 + 0.05997x_1 + 0.00047x_2 - 0.0001x_1^2 - 0.000002x_2^2 - 0.000004x_1x_2 \quad (R^2 = 0.99) \quad (6)$$

As seen here, the regression equations developed for the miscanthus chemical composition have adequately described the process with a lowest correlation coefficient value of 0.96 for carbon content and a highest value of 0.99 for hydrogen, volatile and H/C ratio. The observed and predicted values also indicated that the equations predicted these results very closely. All models were statistically significant at $P < 0.001$. Response surface plots using the regression equations to understand the interaction effect of the process variables on the chemical composition studied. ANOVA (see Table 4) indicated that moisture and carbon content torrefaction time (x_2) and interaction term of torrefaction temperature and time (x_1x_2) was found to be significant. In the case of hydrogen, volatile and H/C ratio linear terms of torrefaction temperature (x_1) and quadratic terms of temperature (x_1^2) were found to be significant.

Table 4. ANOVA of torrefaction process variables.

Process Variable	Chemical Composition				
	Moisture Content (%)	Carbon Content (%)	Hydrogen Content (%)	Volatile Content (%)	H/C Ratio
Linear					
x_1	NS	NS	(+) *	(+) *	(+) *
x_2	(-) *	(-) *	NS	NS	NS
Quadratic					
x_1^2	NS	NS	(-) *	(-) *	(-) *
x_2^2	NS	NS	NS	NS	NS
Interactive					
x_1x_2	(+) *	(+) *	NS	NS	NS

x_1 : Torrefaction temperature (°C); x_2 : Torrefaction time (min); significance measured at $P < 0.1$.

3.3. Bar and Surface Plots

Bar plots were drawn for the actual measured chemical compositional values at different torrefaction temperatures and times. Surface plots were drawn based on the response surface models developed. Moisture content is greatly influenced by torrefaction temperature and time (see Figure 2); a final moisture content of about 0.6% was reached at 350 °C and 120 min. A significant decrease in moisture content of about 82.68% occurred at 250 °C and 30 min. Increasing the temperature to 300 and 350 °C decreased the moisture content further by about 85.82 and 92.47%, respectively. Increased residence times to 60 and 120 min also resulted in similar changes in the moisture content. The surface plot drawn based on the regression equation [see Equation (2)] indicates that the lowest moisture of about 0.6% was achievable at a temperature range of 320–350 °C at 30 min residence time, as is shown in Figure 3.

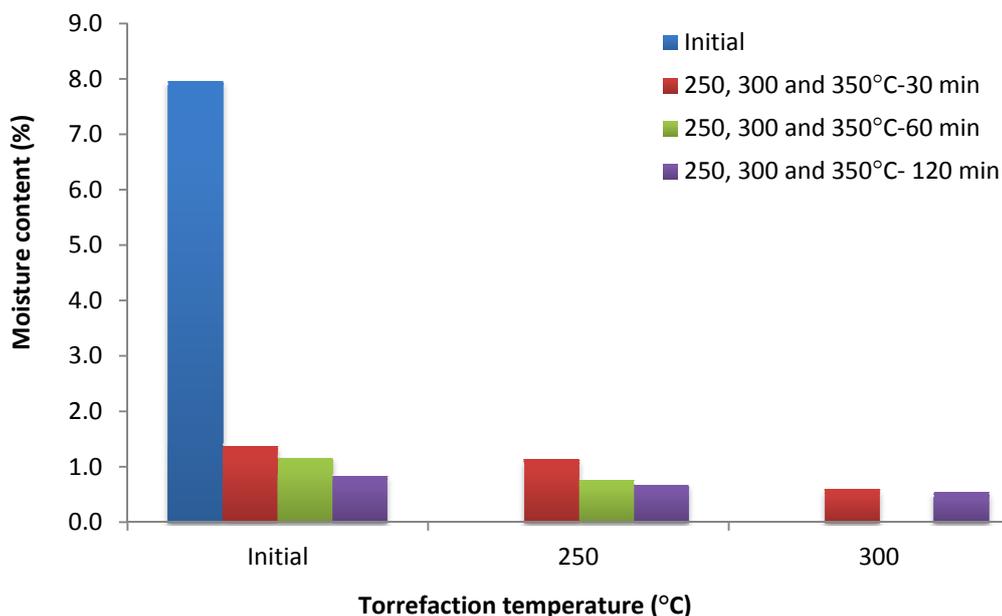
Figure 2. Moisture content of torrefied miscanthus samples.

Figure 3. Effect of torrefaction on moisture content.

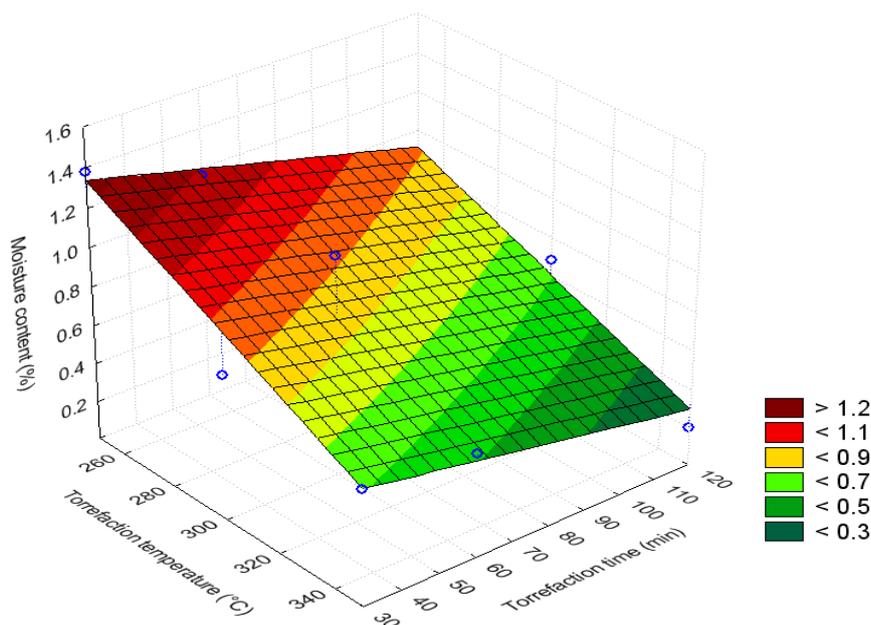


Figure 4 shows the influence of torrefaction temperature and time on carbon content, which relatively increased from about 9%–10.5% with an increase in temperature from 250–350 °C at 30 min of residence time. At 350 °C, further increasing the residence time to 120 min increased the carbon content to about 21%. Figure 5 clearly indicates that a carbon content of >50% was obtained at temperatures >320 °C and at residence times >100 min.

Figure 4. Carbon content of torrefied miscanthus samples.

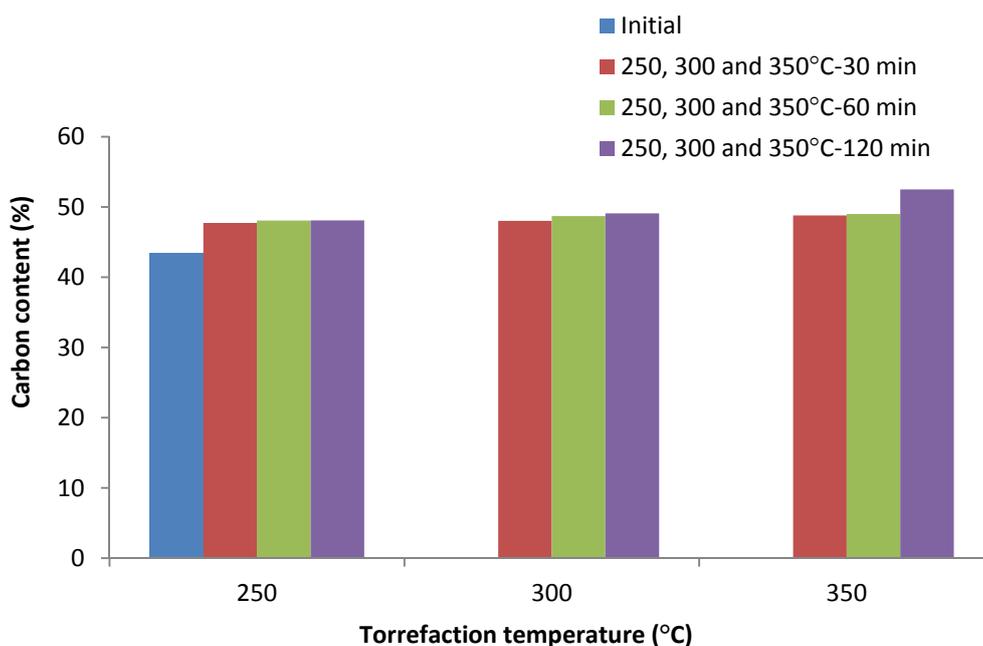
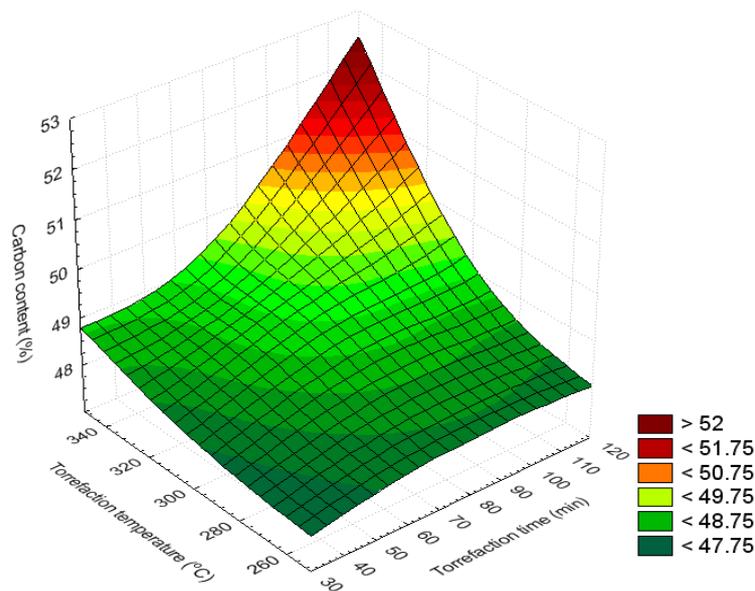


Figure 5. Effect of torrefaction on carbon content.



The relative 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 of 250, 300, and 350 °C and a time of 30 min were 1.70, 5.98, and 54.70, respectively. This decrease was very significant at the higher temperature of >300 °C. Similar results were realized at 60- and 120-minute residence times. A minimum hydrogen content value of 2.44 was observed at a torrefaction temperature of 350 °C and 120 min. The surface plot (not shown) indicated that the torrefaction temperature has a more significant effect compared to residence time.

The effect of torrefaction temperature and time on nitrogen content is shown in Figure 7. The decrease in relative nitrogen content at 250, 300, and 350 °C and 30 min was 3.57, 7.14, and 10.71%, respectively.

Figure 6. Hydrogen content of miscanthus samples.

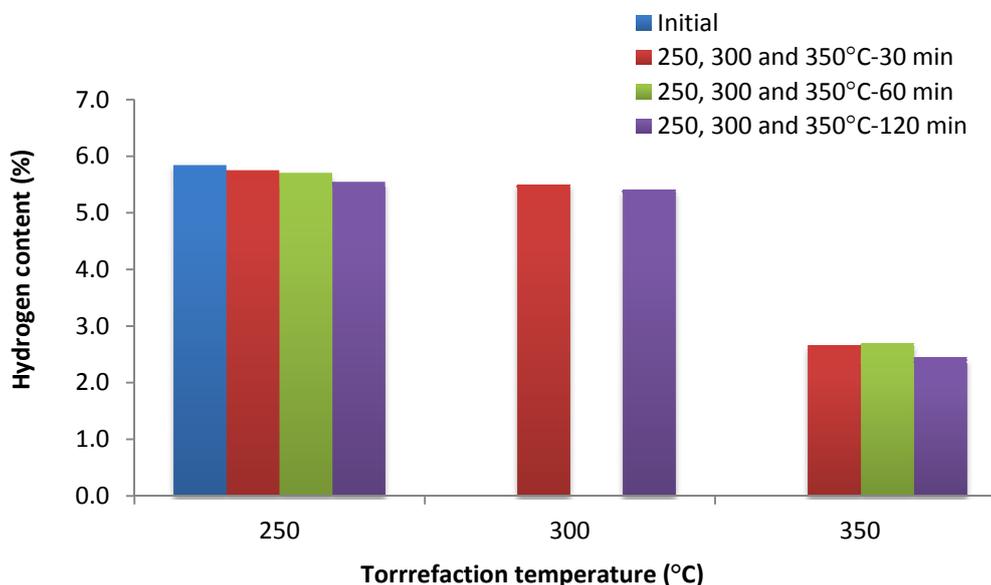
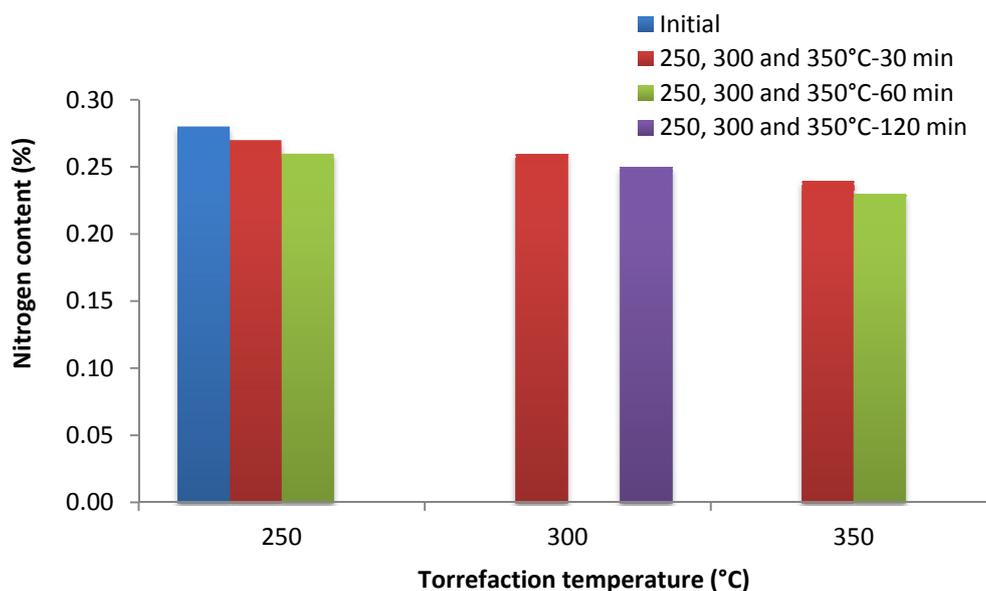


Figure 7. Nitrogen content of torrefied miscanthus samples.

3.4. Volatile Content (%)

Changes in the relative percent volatile content of the material were less than 3.65% at 250 °C, but at temperatures >270 °C, a significant decrease in volatile content values was observed. Further increasing the temperature and residence time to 350 °C and 120 min reduced the volatile content even more significantly (see Figure 8). The decrease at 350 °C for 60 min was 70.45%. The surface plot (see Figure 9) indicated that the volatiles are reduced over 50% at temperatures >320 °C at all residence times (>30 min).

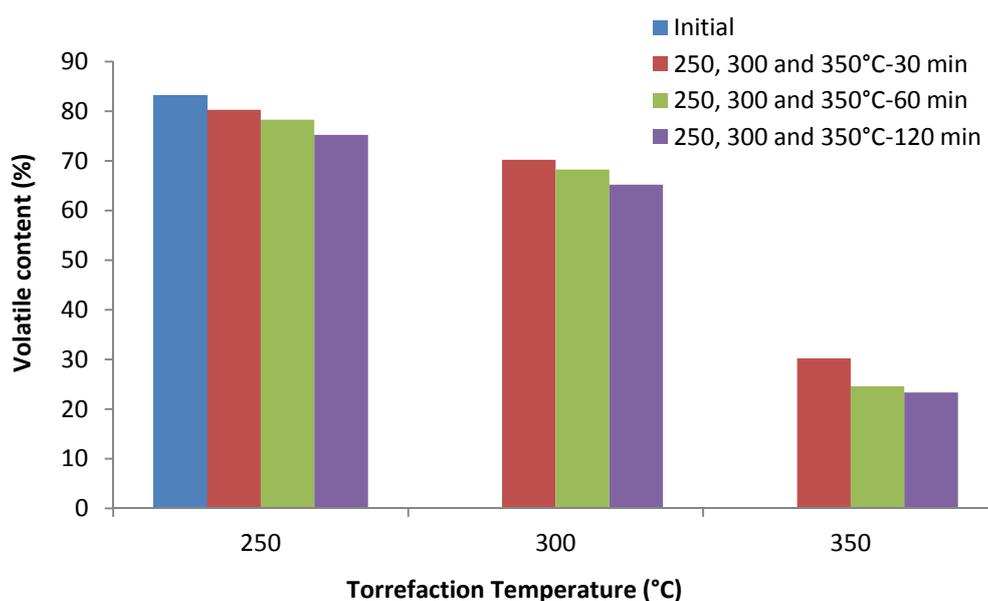
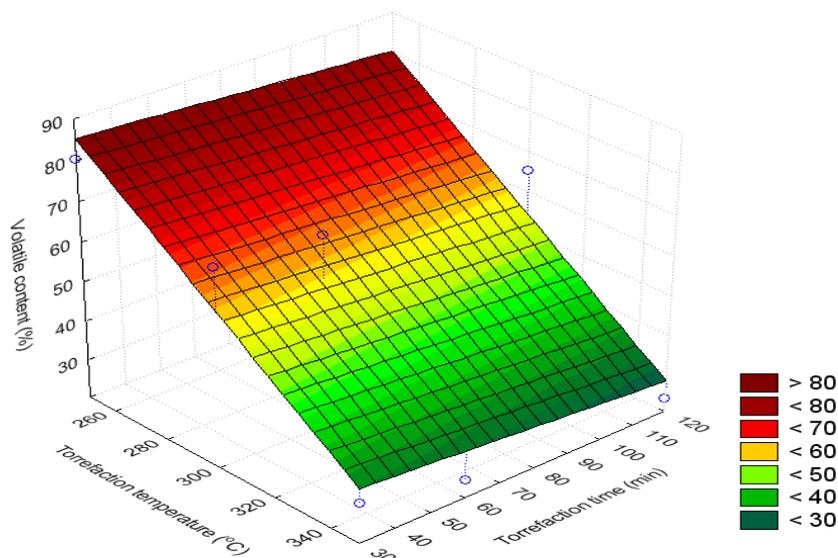
Figure 8. Volatile content of torrefied miscanthus samples.

Figure 9. Effect of torrefaction on volatiles.

3.5. H/C Ratio

Relative H/C ratio content did not decrease significantly at the lowest residence time and temperature. The percent decrease at 250 and 300 °C for 30 min was about 3.65% and 4.44%, respectively, whereas at 120 min, the decrease was about 32.94%. The surface plot (not shown) indicated that H/C ratios of less than one are achievable at torrefaction temperatures >300 °C and at a residence time of >40 min. The H/C value dropped to 0.6% at temperatures >320 °C and at a residence time of >90 min. Relative sulfur values of the torrefied samples decreased by about 50% at 300 °C and were below detection limits at temperatures of 350 °C. Table 5 summarizes these response surface plots.

Table 5. Summary of response surface plots on the chemical composition of miscanthus.

Chemical composition	Torrefaction temperature (°C)	Torrefaction time (min)	Range	Objective
Moisture content (%)	250	30–120	>1.025	Maximum
	300–350	30–120	0.525–0.725	Minimum
Carbon content (%)	320–350	90–120	>49.4	Maximum
	250–350	30–120	47.8–48.6	Minimum
Hydrogen content (%)	250–280	30–120	>4.9	Maximum
	300–350	30–120	2.9–3.9	Minimum
Volatile content (%)	250–300	30–120	80–50	Maximum
	300–350	30–120	50–30	Minimum
H/C ratio	250–280	30–120	>1.4	Maximum
	300–350	30–120	0.6–1.4	Minimum

From the summary of these bar and surface plots, it is very clear that high temperatures (>300 °C) and residence times (>30 min) are required to minimize the moisture content, hydrogen, nitrogen,

volatile, and H/C ratios while maximizing the carbon content. Trends regarding changes in the chemical composition agree with the experimental findings of Sadaka and Negi [30] with wheat straw, rice straw, and cotton gin waste; Zanzi *et al.* [20] with miscanthus, birch, and salix, in addition to wood and straw pellets; and Bridgeman *et al.* [27] in their studies on reed canary grass, wheat straw, and willow.

In their study of reed canary grass and wheat straw torrefaction at 230, 250, 270, and 290 °C for 30-minute residence times, Bridgeman *et al.* [27] also 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 range of 0.525%–0.725% was obtained via torrefaction temperature and residence times in the range of 250–300 °C and 30–120 min.

In their studies on torrefied miscanthus, Zanzi *et al.* [20] made similar observations where increasing the torrefaction temperatures and residence times increased the carbon content and decreased the hydrogen and nitrogen content. Zanzi *et al.* [20] also reported that at torrefaction temperatures of 280 °C for 180 min, the carbon content increased to about 52% from an initial value of 43.5%, while hydrogen and nitrogen content decreased from 6.49% to 5.54% and from 0.90% to 0.65%, respectively. The maximum carbon content was about 2% lower compared to their studies, which may be due to the higher residence time of 180 min used in Zanzi *et al.*'s studies [20]. Nitrogen content, which is about 0.9% in their studies, reduced to 0.65% at 280 °C for 180 min. In our studies, we found the initial nitrogen content to be around 0.25%; this value was reduced by about 3.57%, 7.14%, and 10.71% at 250, 300, and 350 °C for 30 min of residence time, respectively. These values are less than those reported by Zanzi *et al.* [20], where they observed about a 27% reduction at 290 °C for 30 min.

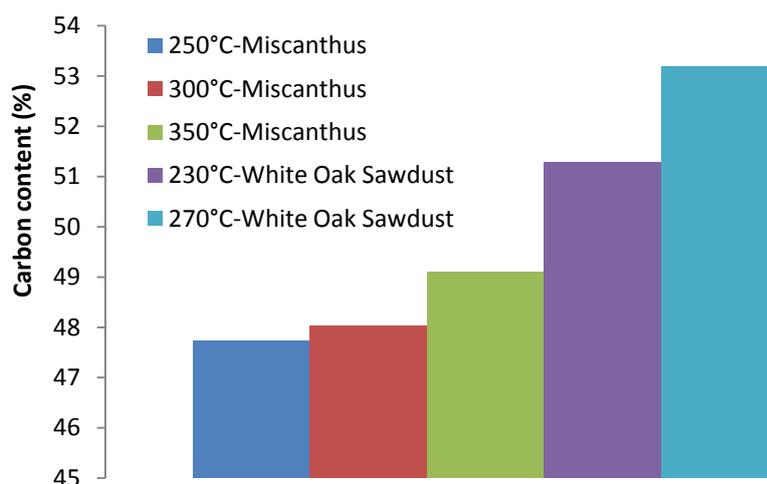
Finally, in their studies on the torrefaction of wheat, rice straws, and cotton gin waste at 200, 260, and 315 °C and 60, 120, and 180 min, Sadaka and Negi [30] observed a significant loss of moisture of about 70.5%, 49.4%, and 48.6%, respectively. The loss of moisture of about 85.82% in the present study matches only with the wheat straw. In their studies on torrefaction of corn stover using a bubbling sand bed, Tumuluru *et al.* indicated that there is a significant change in elemental composition and energy properties [37]. Their results have corroborated with present studies where moisture, hydrogen, and nitrogen content decreased and carbon content increased.

3.6. White Oak Sawdust

The chemical composition of white oak sawdust at two different torrefaction temperatures of 220 and 270 °C is shown in Table 6, indicating that while there is a significant decrease in moisture content of the samples at these temperatures, the volatile, hydrogen, and nitrogen contents have not decreased significantly. Carbon content relatively increased by about 3.5% when torrefied at 270 °C for 30 min. These observations matched closely with the trends obtained by Pach *et al.* [43] in their studies on the torrefaction of birch, where the carbon, nitrogen, and hydrogen values were in the ranges of 53%–56%, 0.17%–0.16%, and 6.2%–5.6%, respectively, for torrefaction temperatures of 230 and 280 °C and at residence times of 60 min. Figure 10 indicates the carbon content changes in white oak sawdust and miscanthus samples. Woody biomass resulted in higher carbon content compared to herbaceous biomass, which can be typically attributed to higher carbon content in the raw samples.

Table 6. Chemical composition changes in white oak sawdust during torrefaction.

S. No	Chemical Composition	220 °C, 30 min	% Change	270 °C, 30 min	% Change
1	Moisture content (% w.b)	2.11	(-75.263	1.79	(-79.01
2	Volatile content (%)	76.90	(- 4.76	66.31	(- 17.88
3	Carbon content (%)	51.28	(+ 1.95	53.10	(+ 3.54
4	Hydrogen content (%)	5.14	(- 3.54	4.67	(- 20
5	Nitrogen content (%)	0.17	0.0	0.16	(- 5.88

Figure 10. Carbon content of torrefied miscanthus and white oak sawdust at 30 min.

4. Discussion

In this study, moisture loss during torrefaction was significant at all torrefaction temperatures and residence times, as observed by Bergman and Kiel [44] and Prins [45]. Loss of moisture can be due to the drying and depolymerization of the hemicellulose, which typically occurs at 225–325 °C. Bridgeman *et al.* [27] indicated that the loss of moisture is mostly due to drying and dehydration reactions between organic molecules. Along with the moisture, there are other organic and inorganic products released, which is indicated by volatile content loss. This typically occurs at torrefaction temperatures of >250 °C. The loss of volatiles increases with respective increases in torrefaction temperatures and residence times as it leads to devolatilization of hemicellulose, cellulose, and lignin.

In general higher torrefaction temperature results in an increase in carbon content and, simultaneously, a decrease in hydrogen and oxygen content which can be due to the formation of water, carbon monoxide, and carbon dioxide. In this study, there is a steep increase in carbon content and a significant decrease in hydrogen content of the torrefied miscanthus samples with increased torrefaction temperatures and times. This results in a decrease in the H/C and O/C ratios, resulting in less smoke and water vapor formation, in addition to less energy loss during the combustion and gasification processes. At lower torrefaction process conditions of 250 and 300 °C with a 30-min residence time, only marginal changes in the hydrogen content of the samples was observed. However, as the temperature increased 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,

sulfur content of the samples was well below the detection limits at higher torrefaction temperatures ($>300\text{ }^{\circ}\text{C}$), which matches Mani's findings on torrefaction of forest residues [46,47].

In addition, the present study indicates that there is significant loss of volatiles, which may include higher energy content volatiles at temperatures $> 300\text{ }^{\circ}\text{C}$. The loss of the higher energy content volatiles may not help in improving the energy properties of the biomass. From the present studies we can conclude that temperatures $>300\text{ }^{\circ}\text{C}$ may not be needed for torrefying biomass to make it suitable for energy applications as there is a significant loss of volatiles, which may increase relative ash content of the biomass. In their review on torrefaction, Tumuluru *et al.* [12] indicated that the torrefaction systems can be made self sustainable by capturing the volatiles lost during torrefaction and reintroducing them as a source of heat. This is typically possible at temperatures $>270\text{ }^{\circ}\text{C}$, where the system is totally exothermic. Studies conducted by Bergman *et al.* [25,26] indicated that at temperatures of $280\text{ }^{\circ}\text{C}$ for 15–30 min will make the process exothermic and self sustainable, if the volatiles are collected and reintroduced as a source of heat. They have also indicated that the torrefied product produced is suitable for thermochemical conversion applications. As observed by Tumuluru *et al.* [37], the bed medium exhibited static charge and became attached to the biomass materials; this effect was minimized by sieving the material before doing the elemental and energy properties analysis. Another alternative to overcome this limitation is changing the bed medium (aluminum oxide) with glass or ceramic beads or silica sand of 3 mm particle size as fluidization medium. As suggested by Tumuluru *et al.* [37], the regression equations with good correlation coefficient values can be a valuable tool for integrated systems optimization and techno-economic analysis. Further studies on understanding the effect of intermediate torrefaction temperatures of 270, 280 and 290°C on the complete proximate and ultimate compositional changes in the biomass will be useful to optimize the process for different end use applications.

5. Conclusions

Changes in chemical composition of both miscanthus and white oak sawdust samples indicated a steep loss of moisture, hydrogen content, and H/C ratio at torrefaction temperatures of $\geq 270\text{ }^{\circ}\text{C}$ and at a time of 30 min. In the case of the miscanthus sample, the volatile content decreased significantly at torrefaction temperatures of $>300\text{ }^{\circ}\text{C}$ and at residence times >30 min. Regression equations developed for the chemical compositions studied have adequately described the changes based on r^2 value. Surface plots developed in this study indicated that torrefaction temperatures of $300\text{--}350\text{ }^{\circ}\text{C}$ and residence times of 30–120 min can help increase carbon content to $>49.4\%$ and reduce moisture, nitrogen, volatile, and H/C ratios from 1.13%–0.6%, 0.27%–0.23%, 79%–23%, and 1.3%–0.6%, respectively. Further torrefaction studies on white oak sawdust at $270\text{ }^{\circ}\text{C}$ for 30 min indicated that moisture, volatiles, hydrogen, and nitrogen content decreased with increased torrefaction temperatures from initial values of 8.53, 80.75, 5.91, and 0.17% to 1.79, 66.31, 4.67, and 0.16%, respectively, whereas the carbon content value increased from 50.28% to 53.10% at the same temperatures and residence times. Our studies also indicated that a bubbling sand bed reactor could be used successfully for the torrefaction of both herbaceous and woody biomass samples by selecting a suitable bed medium.

Acknowledgments

The authors acknowledge Leslie Park Ovard for her valuable contribution to the manuscript and Gordon Holt, Allen Haroldsen, and Lisa Plaster from INL's R&D Publications Support Team for their editorial and graphics creation assistance. This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under DOE Idaho Operations Office Contract DE-AC07-05ID14517. Accordingly, the U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. Government purposes.

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