Biochars Produced from Pressurized Torrefaction: Fuel Properties and Combustion Behaviour

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Abstract - In this paper, the pressurized torrefaction (PT) of miscanthus and the combustion behaviour of the torrefied products were investigated. The torrefaction reactions were conducted in a 600 cm^3 batch autoclave reactor with the operating conditions of temperature, pressure and time varied from 200-300 °C, 10-30 bars and 20-60 minutes, respectively. The key performance metrics of volatile matter reduction, oxygen removal, higher heating value (HHV) enhancement, carbon enrichment and mass/energy yields were evaluated. Our study reported a 4-50% reduction in volatile matter, 4-68% carbon enrichment and a 2-70% oxygen removal in the produced biochars. Furthermore, the higher heating value (HHV) of the biochar ranged from 19.30 ± 0.23 MJ/kg to 34.94 ± 0.65 MJ/kg compared to the raw biomass of 18.86 ± 0.02 MJ/kg. With respect to the influence of pressure, it was found that pressure and secondary reactions played a contributory role in chemical energy preservation, thus leading to high energy yield in the pressurized torrefaction process. Lastly, the derived biochars demonstrated improved characteristics with respect to ignition and burnout temperatures as well as overall combustion performance indices.

Keywords: Biomass, Pre-treatment, Torrefaction, Fuel properties, Combustion

1. Introduction

The sustainable utilization of lignocellulosic biomass for biofuel production is a vital cog in the wheel of sustainability and net zero emission targets. In recent time, thermochemical energy conversion processes, such as pyrolysis, gasification and combustion have been heavily employed to convert biomass wastes to viable fuel products. Nevertheless, there are significant impediments to the economic scale production of biofuels due to inherent undesirable characteristics of biomass, namely high oxygen content, low energy and bulk density, low calorific value and lack of uniformity in their physical and chemical structures[1]. Moreover, the process and efficiency of these energy conversion process are heavily reliant on the feedstock quality. Therefore, pre-treatment is an essential tool in overcoming the aforementioned issues. One such pre-treatment method is torrefaction[2].

Torrefaction involves heating the raw biomass at mild to severe temperatures of 200-300 °C in an anoxic atmosphere[3]. This heating mechanism consequently facilitates the removal of moisture and low-weight organic volatiles while preserving the energetic components of the biomass, thus improving the energy density of the biomass. Additionally, homogenization of the biomass as well as improvement in other fuel properties of the treated biomass such as hydrophobicity, lower oxygen and moisture contents is achieved. Despite these improvements, conventional torrefaction process is still limited in its application. As for any reasonable improvement to be realised in biomass pretreatment, the operation conditions need to be severe, meaning higher temperatures and longer residence times. As such, the performance of conventional torrefaction can be rendered counter-intuitively energy extensive. There have been several reports on the subject of the effectiveness of biomass torrefaction with increasing severity. Devaraja et al.[4] reported that 250°C was insufficient for the torrefaction of two wood biomass types of Rubberwood and Gliricidia, and the effect of residence time was only noticeable at high temperatures. Simonic et al.[5] reported similar observations in their study of mixed wood with the energy yield reduced at higher temperatures and longer residence time despite the increase in the enhancement factor. In other words, conventional

torrefaction is restricted in achieving reasonable enhancement without severe temperatures, which then results in the significant loss of chemical energy through defragmentation of the biomass molecule.

Recently, we investigated torrefaction of biomass under pressure conditions, hence the name "pressurized torrefaction (PT)"[6]. A distinct feature of this laboratory setup is that the released volatiles are not swept away by a purging inert gas as in the case of conventional torrefaction. Therefore, an autogenous pressure is generated through the confinement of the volatiles in the batch reactor and the thermal expansion of the generated gases. This facilitates further secondary reactions between the volatiles and solid biomass, allowing further dehydration and deoxygenation reactions compared to conventional torrefaction occurring at atmospheric pressure. Tong et al.[7] studied the effect of pressure and secondary reactions and found that they both synergistically contributed to HHV enhancement, oxygen removal and cellulose reduction in the biomass even at low temperatures of 200 °C. Other studies[8,9]have highlighted the advantages and pitfalls of pressurized torrefaction; howbeit, there lies a dearth of studies investigating the effect of operating conditions on the fuel properties of the derived product. Furthermore, the behaviour of the torrefied biomass in further thermochemical processes, namely gasification, pyrolysis and combustion, remains unclear.

Miscanthus (MIS) is one of the most wildly cultivated energy crops in Europe due to its rapid growth and favourable carbon balance. Nevertheless, it is still characterised by low bulk density, low energy density as other biomasses, which ultimately lowers thermal conversion efficiency and limits its utilization[10]. From that standpoint, this work aims to investigate the fuel properties and combustion behaviour of torrefied biomass derived from Miscanthus in pressurised torrefaction to have a more in-depth understanding of the commercial ability of this process.

2. Material and Method

The raw MIS biomass sample was harvested and collected from Southwest Germany. The samples were ground and sieved to 90-212μm and then dried at 105 ℃ under vacuum for more than 24 hrs. The elemental analyser (Vario CHNEL-2) was used to determine the elemental composition of the raw and torrefied samples. The proximate, ultimate analyses and ash composition of the samples are shown in **Table 1**.
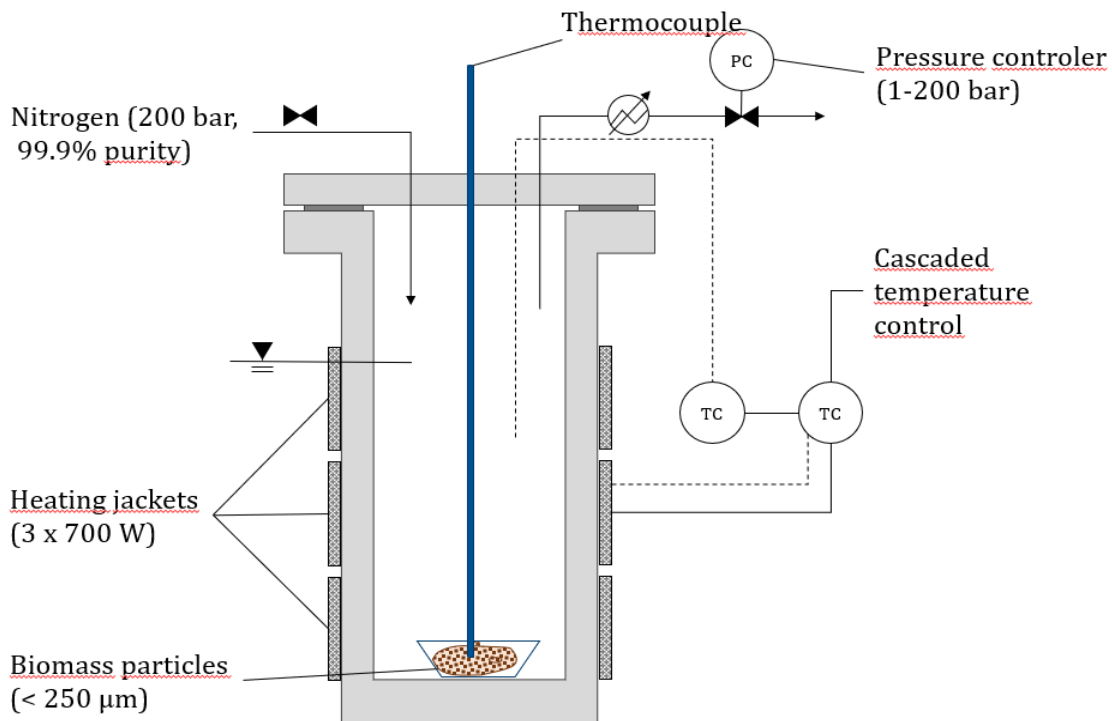

Fig. 1: The schematics of a batch autoclave

The pressurized torrefaction was performed in a 600 cm^3 batch autoclave reactor (Parr 4560 batch reactor) as illustrated in **Fig 1**. About 18 g of the dried raw biomass was placed in a crucible, which then placed into the autoclave. The autoclave was then sealed and sufficiently purged and pressurized with nitrogen at an initial pressure. For a target temperature of 250 °C, the initial pressures of 2, 4,10 bars were needed to achieve a final pressure of 10, 20 and 30 bars, respectively. For 300 °C, these initial pressures are 0.5, 1 and 3.5 bars. The sealed autoclave was then heated to the targeted temperature at a heating rate of 7 °C/ min. After maintaining the target temperature for the residence times of interest, that is, 20, 40 and 60 min, the heating jacket is removed immediately and the autoclave is immersed in a water bath for rapid cooling, so as to immediately stop the reaction. The cooled gases are then slowly released from the autoclave into a gas bag, and the torrefied samples are cooled to room temperature and weighed. The mass and energy yield are then calculated according to equations 1 and 2.

In this paper, the nomenclature of the torrefied biomasses is as follow: the miscanthus sample derived from torrefaction at 200 °C at a pressure and residence time of 10 bars and 60 min is designated as MIS-200-10-60. For the combustion reaction, a thermogravimetric analyser (Netzsch STA 4495) was used. Approximately 2 mg of the sample was placed in a platinum crucible and heated from room temperature to 900°C at a heating rate of 10 °C/min in the presence of synthetic air at a flow rate of 25 ml/min.

$$Mass\ yield\ (\ \%\ ) = \frac{Mass\ of\ torrefied\ biomass}{Mass\ of\ raw\ biomass} \tag{1}$$

$$Energy\ yield\ (\ \%\ ) = \frac{Mass\ yield\ \times HHV\ of\ torrefied\ biomass}{HHV\ of\ raw\ biomass} \tag{2}$$

3. Results and Discussion

3.1. Fuel Analysis

The proximate analysis collated in **Table 1** highlights that as temperature increased, there were notable reductions in the volatile matter contents of the torrefied biomass, and conversely, an increase in fixed carbon content. In fact, there was a reduction of 4.28-50.25% in the volatile matter with the different operation conditions. Among the three studied temperatures, the largest reduction and increase in volatile matter and fixed carbon contents were noticed at 300 °C. With respect to the ultimate analysis, a similar trend with carbon percentage was noticed, where an increasing temperature resulted in improvement of the carbon content of the torrefied biomass. On the other hand, the oxygen removal capabilities of the pressurized torrefaction method were clearly highlighted. Significant deoxygenation occurred during the pressurized torrefaction ranging from 2-70% oxygen removal in the produced biochars at mild to harsh torrefaction conditions.

One of the main objectives of torrefaction is to achieve enhancement in the higher heating values (HHV). The HHV is an intuitive parameter in discerning the extent of the energy densification of the torrefied biomass after torrefaction and was therefore calculated using the least-square regression (OLS) method[11]. As shown in **Table 1**, there was invariably an improvement in the HHV of solid biomass with an increase in temperature. The largest HHV achieved throughout the pretreatment method was 34.94 MJ/kg, which correlates to an 85.3% improvement from that of the raw biomass. Furthermore, these values resemble the heating values of different types of coal that have been used in plasma gasification[12].

The Van Krevelen diagram displaying the H/C and O/C ratios of the torrefied biomasses in **Fig 2** further consolidates the argument of coalification. With an increase in the thermal severity of the torrefaction process, that is, an increase in temperature, the greatest carbonization of the samples was attained. The sample that was torrefied at 300 °C at 30 bars and 60 mins had qualities that were similar to that of sub-butiminous coal. Even at the moderate temperature of 250 °C, there was a notable amount of coalification, as the samples torrefied at this temperature had similar characteristics to those of low-ranking coal.

Table 1: Proximate and Ultimate Analyses of Raw and Torrefied Miscanthus

Samples	Proximate Analysis				Ultimate Analysis (wt%, dry basis)					
	Moisture (wt%)	VM (wt%, db)	FC (wt%, db)	Ash (wt%, db)	C	H	N	S	O (diff)*	HHV (MJ/kg)
MIS	4.87 ± 0.09	81.45 ± 0.49	16.26 ± 0.80	2.29 ± 0.31	47.90 ± 0.04	5.33 ± 0.05	0.35 ± 0.02	0.10 ± 0.00	46.33 ± 0.07	18.86 ± 0.02
MIS_200_20_60	4.73 ± 0.63	77.96 ± 0.86	20.28 ± 0.85	1.76 ± 0.00	49.84 ± 0.42	4.30 ± 0.26	0.51 ± 0.00	0.07 ± 0.01	45.29 ± 0.69	19.30 ± 0.23
MIS_250_10_20	4.09 ± 0.66	69.16 ± 2.04	28.46 ± 1.97	2.38 ± 0.08	54.71 ± 1.42	5.03 ± 0.09	0.66 ± 0.03	0.11 ± 0.03	39.49 ± 1.50	21.49 ± 0.64
MIS_250_10_40	4.76 ± 0.15	65.67 ± 0.43	31.93 ± 0.31	2.39 ± 0.12	56.83 ± 0.41	5.16 ± 0.01	0.60 ± 0.01	0.08 ± 0.00	37.33 ± 0.41	22.47 ± 0.19
MIS_250_10_60	5.49 ± 0.83	64.16 ± 0.48	33.35 ± 0.36	2.49 ± 0.12	58.67 ± 0.00	5.10 ± 0.07	0.65 ± 0.01	0.08 ± 0.00	35.51 ± 0.08	23.24 ± 0.06
MIS_250_20_60	4.50 ± 0.42	54.90 ± 2.39	42.13 ± 2.19	2.97 ± 0.21	63.94 ± 1.90	4.97 ± 0.10	0.71 ± 0.00	0.09 ± 0.02	30.30 ± 1.79	25.56 ± 0.80
MIS_250_30_60	7.42 ± 0.16	58.34 ± 4.45	38.55 ± 4.34	3.11 ± 0.11	63.07 ± 3.09	5.16 ± 0.17	0.69 ± 0.05	0.05 ± 0.00	31.03 ± 1.79	25.34 ± 1.32
MIS_300_10_60	5.69 ± 0.63	40.90 ± 0.50	55.25 ± 0.44	3.85 ± 0.06	72.97 ± 0.05	4.45 ± 0.07	0.60 ± 0.03	0.09 ± 0.02	21.89 ± 0.02	29.36 ± 0.08
MIS_300_20_60	5.86 ± 0.21	43.07 ± 1.06	52.94 ± 0.93	3.99 ± 0.13	70.35 ± 0.38	4.75 ± 0.11	0.77 ± 0.02	0.06 ± 0.00	24.07 ± 0.26	28.46 ± 0.05
MIS_300_30_60	6.15 ± 0.73	40.52 ± 0.77	55.91 ± 0.85	3.57 ± 0.08	80.35 ± 0.08	5.30 ± 0.38	0.62 ± 0.05	0.06 ± 0.00	13.67 ± 0.25	34.94 ± 0.65

VM: Volatile Matter; FC: Fixed Carbon; *O% was calculated by difference

This lends credence to the favourable performance of pressurized torrefaction even at milder temperature conditions. Xue et al[10] torrefied the same species of miscanthus at 270 degrees Celsius for 30 mins using normal torrefaction and was only able to achieve an oxygen reduction and a carbon increase of 19% and 20%, respectively. In addition, the HHV only increased to 21.6 MJ/kg. The results at 250 degrees at the lowest pressure are similar to these results.

3.2. Influence of temperature, pressure and residence time on mass and energy yields

As aforementioned in the previous section, an increasing temperature invariably had a positive effect on the volatile matter reduction, carbon content, deoxygenation and HHV enhancement. However, increasing the temperature through normal torrefaction conventionally leads to a decrease in mass yield, which subsequently reduces the energy yield due to prominence of decarboxylation, dehydroxylation and depolymerization reactions[13]. Considering this reality, pressurized torrefaction is proposed as a means of overcoming the issue of energy loss by preserving the chemical energy through secondary reactions. With these secondary reactions, such as, aromatization polymerization, the emergence of a more stable biochar molecule is facilitated; however, simultaneously enhancing oxygen removal by means of dehydration of the cellulose and hemicellulose units[14]. The energy yield remains negligibly unchanged despite the significant mass losses that is concomitant with higher temperature conditions.
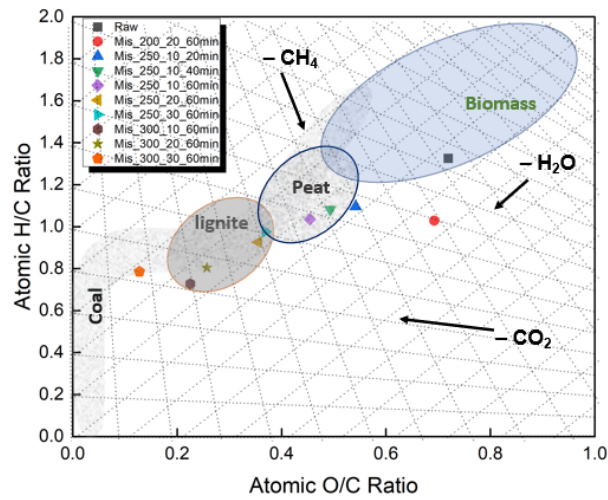
Fig. 2: The H/C and O/C ratios of the biochars

Fig 3 illustrates the mass and energy yield of the torrefied products formed under the varied operating conditions of temperature, pressure and time. It is clearly observed that the highest energy yields were correlated to the samples produced at 30 bars. This implies that the final pressure, a proxy of volatile concentration led to agglomeration of the biomass fragmented units. As expected with torrefaction, the mass yield decreased with elevating temperatures from 200 to 300°C; however, a higher pressure at the same temperature and residence time maintained the energy yield like that of the untreated product, indicating a high extent of chemical energy preservation.
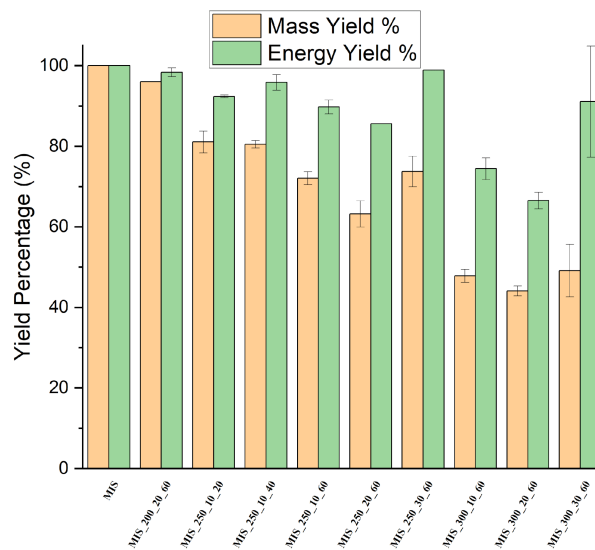

Fig. 3: The mass and energy yields of raw and torrefied samples

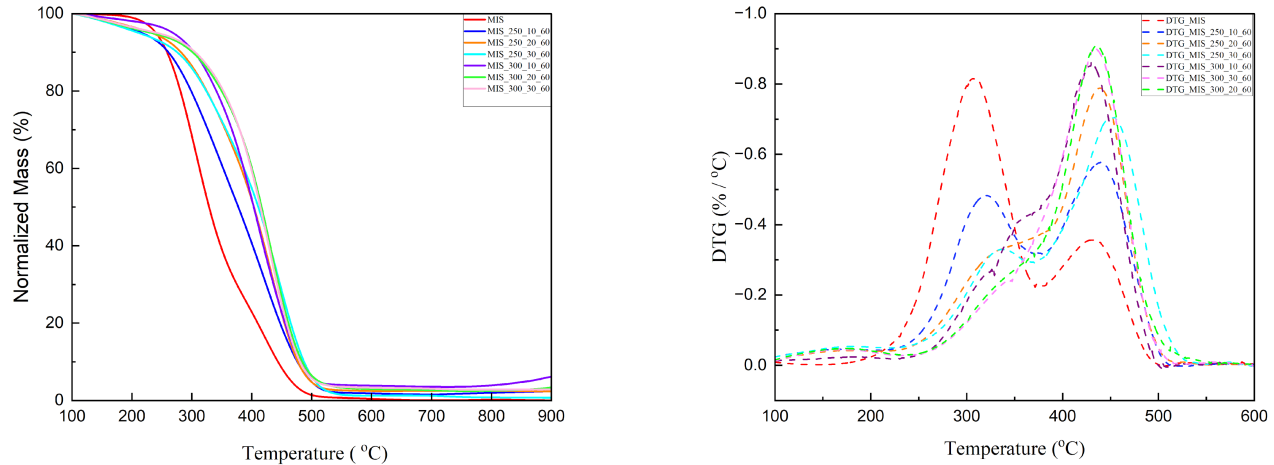## 3.3. Combustion Behaviour

Fig. 3: The TGA and DTG curves of the 250 and 300ºC

In this section, the thermogravimetric analyser (TGA) was utilized to examine the combustion behaviour of the torrefied biomass. The raw and torrefied biomas at 250 °C and 300 °C with a residence time of 60 min with a varied pressure of 10, 20 and 30 bar were selected. The objective is to analyse the biomass decomposition throughout combustion by highlighting the characteristic parameters derived from the TGA and DTG curves. The TG and DTG curves for raw and torrefied miscanthus during combustion are demonstrated in **Fig 4,** and the combustion characteristic data is extracted from the curves and is summarized in **Table 2.** A similar characterization was done in this study of co-combustion characteristics of tobacco stem and butiminous coal [15]. The ignition temperature (T_i), burnout temperature (T_b), peak temperature during devolatilization ($T_{max,d}$), peak mass loss during devolatilization ($m_{max,d}$), peak temperature during char combustion ($T_{max,c}$), and peak mass loss during char combustion ($m_{max,c}$), mass loss during devolatilization and char combustion (Δm_d) and (Δm_c) were all determined.

Table 2: Combustion characterizing parameters of raw and torrefied Miscanthus.

Combustion Parameters	MIS	MIS_250_10	MIS_250_20	MIS_250_30	MIS_300_10	MIS_300_20	MIS_300_30
T_i (ºC)	177	225	234	241	250	265	265
T_b (ºC)	497	513	517	535	504	553	517
$T_{max,d}$ (ºC)	306	321	327	340	356	359	348
$T_{max,c}$ (ºC)	432	441	442	454	429	435	435
$m_{max,d}$ (-%/ºC)	0.81	0.48	0.33	0.33	0.43	0.29	0.24
$m_{max,c}$ (-%/ºC)	0.35	0.58	0.78	0.71	0.86	0.91	0.90
DTG_{max}(-mg/r	0.15	0.11	0.16	0.17	0.22	0.22	0.23
DTG_m(-mg/m	0.058	0.060	0.066	0.076	0.094	0.075	0.092
Δm_d (%)	69.30	41.06	36.70	28.22	31.03	16.32	12.05
Δm_c (%)	29.33	51.69	55.69	63.79	61.67	74.35	78.50

D_i x 10^{-6} (mg/min · ^{o}C^2	2.76	1.24	0.87	0.98	1.25	0.72	0.67
D_c x 10^{-10} (mg^2(min · ^{o}C^3	5.59	2.54	3.73	4.16	6.56	4.25	5.82

The combustion performance can be assessed using the ignition index (D_i) and comprehensive performance index (D_c). D_i represents the fuel ignition performance, which indicates how quickly or slowly the biochar is ignited, whereas D_c clarifies the combustion performance[16]. The larger values of D_c imply a more vigorous combustion, and consequently a faster char burnout. From **Fig 4**, it is observed the combustion process can be divided into two main stages, which is strongly related to the volatile matter and fixed carbon contents of the solid fuel. The first stage is the devolatilization and combustion of the released volatile matter, while the second is the combustion of the residual char. The devolatization peaks in the raw and samples torrefied at 250°C are evident; however, this peak is tenuous in the samples torrefied at 300°C due to their low volatile matter contents. The peaks corresponding to the residual char combustion are conspicuous for all samples. With regards to the combustion characteristics, it is quite apparent that the ignition temperature T_i of torrefied char is higher than that of the raw miscanthus. The higher the ignition temperature, the lower the likelihood of spontaneous ignition, and is therefore a direct measure of safety during storage. Furthermore, the ignition temperature increases with pressure. Besides the T_i, the ignition indices (D_i) further consolidated this observation as the torrefied biomass displayed lower indices as the pressure was increased, barring the sample torrefied at 250°C and 30 bars. The burnout temperature of the torrefied biomass were slightly higher than that of the raw biomass. Additionally, this burnout temperature increased with increasing pressure at moderate temperature. As for the combustion performance indices, the values increased from 10 to 30 bars for the samples torrefied at 250 ^{o}C. Meanwhile, all the samples torrefied at 300°C possessed higher values than those torrefied at 250°C. These results suggest that pressurized torrefaction improves the combustion characteristics at high temperatures. In addition, the significant decrease in volatile matter observed in the torrefied biochar contributes to a more stable flame during combustion[17].

4. Conclusion

Pressurized torrefaction facilitates significant improvement in the volatile matter reduction, oxygen removal, HHV enhancement and carbonization of miscanthus energy crop. At the most severe conditions of temperature, residence time and pressure (300°C, 60 mins and 30 bars), the highest reduction in volatile matter and oxygen contents of 50.2% and 70.5% were attained, respectively. Additionally, the heating value of the raw miscanthus at 18.86 ± 0.02 MJ/kg increased to the highest value of 34.94 ± 0.65 MJ/kg over the course of treatment. A key performance advantage of pressurized torrefaction is the influence of secondary reactions. This resulted in a significant increase in the fixed carbon content of the torrefied biomasses at moderate to high temperatures, thereby achieving a maximum value of 55.91 ± 0.85% compared to that of the raw miscanthus o 16.26 ± 0.80%. Moreover, pressure played a pivotal role in the preservation of chemical energy leading to high energy yields even at harsh temperatures. Lastly, pressurized torrefaction reduces the ignition spontaneity of torrefied biomass and improves key combustion characteristics, thus supporting safe storage and transportation of treated biomass and subsequent thermal conversion.

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