

Article

Torrefaction of Agricultural and Wood Waste: Comparative Analysis of Selected Fuel Characteristics

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Abstract: Abundant biomass is a potential energy source. However, it possesses several challenges when considered for energy applications. Torrefaction, a thermal pretreatment process can improve the properties of biomass as energy source. This study focused on comparing effect of torrefaction operating parameters on agricultural and wood wastes properties as fuel. The physiochemical properties, composition, moisture-biomass interaction and ash melting behavior were determined. The result show that higher torrefaction temperature and longer residence time increased lignin content, reduced hemicellulose and cellulose content. The moisture uptake of torrefied biomass was reduced in the range 2.47–9.94% compared with raw biomass depending on torrefaction temperature that indicate torrefied biomass was more hydrophobic than raw biomass. The moisture adsorption isotherm curve shows type II isotherm based on the Brunauer-Emmett-Teller's (BET) classification and was best described by the Oswin model. In addition, torrefaction treatment showed significant influence on the melting behavior of the biomass ash. Especially for agricultural wastes, the fouling tendency shifted from serious range to low range with torrefaction treatment. Torrefaction showed promise for improving fuel characteristics of the studied biomass.

Keywords: ash melting behavior; biomass composition; fouling tendency; moisture adsorption isotherm; torrefaction



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1. Introduction

Under its climate plan '2050 climate neutral Europe', EU is aiming to reduce greenhouse gas emissions by 80% by 2050 compared with their level in 1990 [1]. Extensive usage of fossil fuels, such as coal, is one of the major reasons for increased greenhouse gas emissions in the environment [2]. In 2019, the global primary energy production from coal was 27% of total energy production [3]. The total coal production worldwide was 7921 Mt [4]. From that the EU28 region's contribution was 375 Mt [4]. Thus, replacing the coal with renewable resources is one of the options to achieve climate neutral Europe. In that line, an alliance of 20 nations, for example Finland, Denmark, Germany, and France committed to phase out coal from their energy mix by 2030 [5].

One alternative to using fossils is utilization of renewable resources, such as biomass. Today, biomass is already acting as a primary energy source in several parts of the world. However, using wood from forest in large quantities for energy applications is also under question because of the sustainability aspects [6,7]. On the other hand, agricultural activities produce large quantities of organic residues. In 2016, the estimated total of crop residues generated in EU-28 region was around 168 million dry tons [8]. According to Statistics Estonia [9], the area for barley cultivation in Estonia was in the range of 102,487 to 138,485 ha for the last 5 years (2016–2020). Roughly around 2.79 tons of straw can be produce per

ha of barley cultivation [10]. Thus, the potential for barley straw production in Estonia is around 285,000 tons for the last 5 years. Handling such large quantities of agricultural residue is also a global concern. Thus, these crop residues could be used as an alternative to the fossil resources to produce energy.

Although biomass is available at large quantities, its direct application in energy and material production is not feasible due to several issues associated with it. As listed previously by several authors [11–13], these issues include: (1) high moisture content (2) fibrous nature (3) hydrophobicity (4) high ash content (5) higher volatile content, and (6) lower bulk density. In order to address these issues, biomass needs to be pre-treated. Selection of the suitable pretreatment method depends on the end application of biomass and desired products.

Recently, torrefaction has evolved as a biomass pretreatment with an aim of improving the fuel characteristics of the biomass in a view of thermal conversion processes. In general, torrefaction is a thermal pretreatment, which is mainly carried out in the temperature range of 200–300 °C for a longer period (i.e., 30 to 60 min) in an inert environment [14]. Torrefaction is mainly interesting because it can improve the biomass properties to a level competing with coal. Torrefied biomass could be used either as an alternative to coal or in co-combustion with coal [15]. Torrefied biomass can also be used as a feedstock in the pyrolysis [16] and gasification [17] processes. Additionally, torrefied biomass also can be used as adsorbent [18–21] and for soil amendment [22,23]. The yield of torrefied biomass depends on the operating temperature and residence time. Previously, Manouchehrinejad et al. [24] observed a torrefied biomass yield of 84.69 and 56.46 wt.% for torrefaction temperature of 250 and 290 °C, respectively, for wood waste. The solid yield from torrefied agricultural waste (barley straw) at 200–240 °C during 20–60 min was in the range of 50.1–90.1% [19].

Previously, several researchers have studied the influence of torrefaction operating parameters on the properties of torrefied biomass. For example, Lin et al. [25] studied torrefaction of *Washingtonia filifera* and *Sterculia foetida* in the temperature range of 210 to 300 °C with a residence times of 30 min and 60 min. The authors observed rise in the heating value by 33% for *Washingtonia filifera* biomass. In a study on the effect of torrefaction on oil palm empty fruit bunch, Nyakuma et al. [26] observed that the hard grove grindability index increased from 53.66 for raw biomass to 108 for the torrefaction temperature of 300 °C. In another study, Wilk et al. [27] studied the co-torrefaction of woody biomass and sewage sludge and reported that torrefaction did not have a significant impact on sewage sludge when compared with wood waste. Wang et al. [11] compared the influence of torrefaction treatment on different parts of Norway spruce i.e., stem wood, stump, and bark. The authors observed that hemicellulose content reduced to less than 1% during the torrefaction at 300 °C for 60 min, for all the biomass samples. They also observed that the influence of torrefaction treatment on the grinding energy requirement of bark is limited compared to that for stem and stump wood. In an another study, Zhang et al. [28] compared the moisture uptake of soybean straw and pine wood pellets before and after torrefaction treatment and reported that the hydrophobicity of the pellets increased with torrefaction treatment. A recent study reported that torrefaction treatment reduced the slagging index and increased the fouling index of rubberwood biomass ash [29].

Previous studies on biomass torrefaction have focused mainly on the properties like heating value, proximate and ultimate analysis, energy and mass yields. However, the influence of torrefaction treatment on biomass components, biomass-water interaction and ash melting behavior are the least studied. The ash related issues such as fouling, bed agglomeration, slagging and corrosion are some of the challenges in biomass combustion, and at the same time combustion is the primary intended application of torrefied biomass. Thus, it is important to understand the influence of torrefaction treatment on the ash melting behavior during combustion. At the same time, understanding the influence of torrefaction treatment on biomass fibers and quantifying them could also be helpful when torrefied biomass is considered for the applications other than combustion process. Similarly, it is also important to understand the influence of torrefaction treatment on biomass-water

interactions for the better planning of storage and logistics of torrefied biomass. The growth conditions of the biomass species and the variation in torrefaction operating systems (batch or continuous) can also have significant impact on the properties of the torrefied biomass. In that regard, this study focused on understanding the influence of torrefaction operating parameters on physiochemical properties, chemical composition, ash melting behavior and hydrophobicity of agricultural wastes and wood wastes from Estonia.

2. Materials and Methods

2.1. Materials

In this study, agricultural wastes—barley straw (BS) and cumin stalks (CS)—were selected as raw materials. The forestry wood waste (WW) was also studied in order to make a comparative analysis between agricultural wastes and woody biomass. The selected agricultural wastes were collected from the fields located near the Tartu city, Estonia. The selected forestry wood waste is a mixture of different species, such as spruce, birch, and pine and was supplied by Sarles OÜ, Tartu, Estonia in the form of chips of varied size. The selected biomass was chipped using Retsch SM100, (Retsch GmbH, Haan, Germany). The biomass was open dried for around 2 weeks prior to experiments. It is worth to note that the forestry biomass had been in the open environment for long time before collected for experiments.

2.2. Torrefaction Experiments

A continuous torrefaction reactor system presented in Figure 1 was used to carry out the torrefaction experiments. The reactor was heated with ceramic heaters. The heater temperatures were controlled using PID controllers. The temperature data was recorded continuously using model TC-08 of Picotech, United Kingdom. The residence time of the biomass inside the reactor was controlled by controlling the rotational speed of the screw through frequency controllers. Nitrogen gas was used to maintain the inert environment. The nitrogen flow rate was controlled using flow meter (Vögtlin Instruments GmbH, Herne, Germany). Initially, the reactor was filled with nitrogen at a rate of $10 \text{ L} \cdot \text{min}^{-1}$ for 10 min. Later, nitrogen flow was reduced to $5 \text{ L} \cdot \text{min}^{-1}$ throughout the experiment. Torrefaction was carried out at three different temperatures i.e., 225, 275 and 300°C . Two residence times of 30 and 60 min were used. At the end, torrefied biomass was collected and stored in air tight plastic containers for further analysis. The volatiles released during torrefaction were condensed using water cooled condenser to produce torrefaction condensate. The uncondensed volatiles were released to exhaust system. The torrefied biomass was labeled as TBS for torrefied barley straw, TCS for torrefied cumin stalks, and TWW for torrefied wood waste.

2.3. Analytical Methods

2.3.1. Heating Value

The higher heating value (HHV) of the biomass before and after the torrefaction was measured using IKA calorimeter C5000 based on ISO 1928:2009. Prior to analysis, biomass samples were dried at $105 \pm 2^\circ\text{C}$ to moisture free. For each analysis, around 0.5 g of the ground biomass with particle size less than 1 mm was loaded into a glass crucible. The cotton thread was attached to the sample in order to initiate the ignition. Then, crucible was placed in a closed container (bomb). The pure oxygen at 30 bar was used to combust the sample. The analysis was carried in duplicates for each sample and average value is presented in $\text{MJ} \cdot \text{kg}^{-1}$.

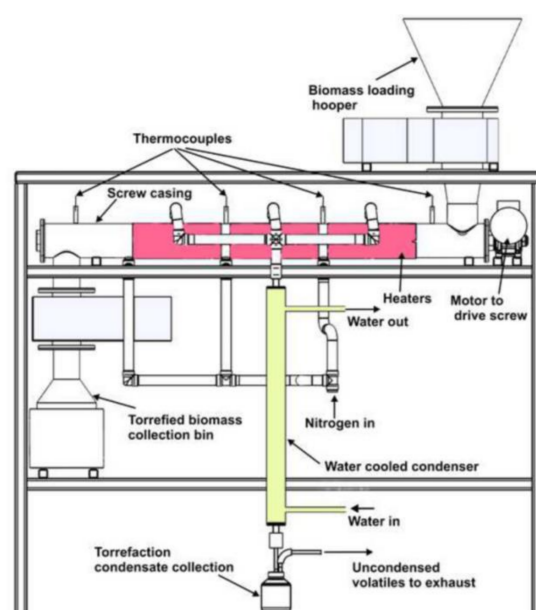


Figure 1. Torrefaction reactor system.

2.3.2. Elemental Analysis

Around 100 mg of the ground and moisture free biomass was encapsulated using tin foil. The carbon, hydrogen, nitrogen, and sulfur was determined using Elementar Vario Macro Cube based on EVS-EN ISO 16948:2015. The oxygen content was calculated as a difference ($O = 100 - (C + H + N + S)$).

2.3.3. Composition Analysis

The fiber composition in terms of cellulose, hemicellulose, and lignin was determined using ANKOM 2000 analyser (ANKOM Technology, Macedon, NY, USA) as outlined in the procedure by ANKOM Technology. For neutral detergent fiber (NDF) and acid detergent fiber analysis (ADF), 0.45–0.5 g of ground raw and torrefied biomass was placed in the filter bag. Using a heat sealer, the filter bag was completely closed. The sample was spread uniformly inside the filter bag to avoid sample clumping. The bag suspender trays were placed in the vessel and the solution was added. Extraction followed by rinsing was run automatically. For each run, two blank bags were also placed in the tray.

When the process was finished, the bag was dried at 105 °C and the final weight was measured. The percentage of ADF and NDF were calculated using Equation (1).

$$NDF/ADF (\%)(as - received basis) = \frac{(W_3 - (W_1 \times C_1))}{W_2} \times 100 \quad (1)$$

where, W_1 = initial bag tare weight, W_2 = initial sample weight, W_3 = dried weight of bag with fiber after extraction process, and C_1 = blank bag correction

After ADF determination, the dried bags were placed in a 3 L beaker and submersed in 72% H_2SO_4 . After 3 h, the bags were removed from the solution and rinsed with tap water to remove all acid. The rinsing process was repeated until the pH of the bag was neutral. The bags were dried at 105 °C and then weighed. The process was followed by ashing process. The acid detergent lignin (ADL) was calculated based on Equation (2).

$$(\%)(as - received basis) = \frac{(W_3 - (W_1 \times C_1))}{W_2} \times 100 \quad (2)$$

where, W_1 = initial bag tare weight, W_2 = initial sample weight, W_3 = weight of organic matter loss during ashing, C_1 = ash corrected blank bag

NDF is considered as the sum of hemicellulose, cellulose, and lignin. ADF is considered as cellulose and lignin. ADL is considered as lignin. The hemicellulose, cellulose, and lignin contents were calculated based on Equations (3)–(5).

$$\text{Hemicellulose} = \text{NDF} - \text{ADF} \quad (3)$$

$$\text{Lignin} = \text{ADL} \quad (4)$$

$$\text{Cellulose} = \text{ADF} - \text{ADL} \quad (5)$$

2.3.4. Moisture Analysis

The moisture contents of the raw and torrefied biomass were determined using the Kern MLS-50-3D (Kern & Sohn GmbH, Balingen, Germany) moisture analyzer.

2.3.5. Hydrophobicity

The moisture uptake of both, raw and torrefied biomass were tested using a climate chamber Rumed FN400HR (Rubarth Apparate, Laatzen, Germany). Prior to experiments, the biomass was oven-dried at 105 ± 2 °C to moisture free. Then, samples were loaded into a glass dish and placed into a climate chamber. The climate chamber was operated at relative humidity (RH) of 95% and temperature of 30 for 3 days. At the end, the weight of the samples was measured and the relative weight gain by the samples compared to the initial sample weight represents the moisture uptake of the samples [30].

2.3.6. Moisture Adsorption Isotherm

Before experiments, the biomass oven-dried at 105 ± 2 °C to moisture free. Then, samples were loaded into a glass dish and placed into a climate chamber. The climate chamber was operated at a different RHs, 95%, 75%, 50%, 30%, and 20% and temperature of 30 °C. The weight of the biomass was monitored until the equilibrium was reached.

The experimental data were fitted using three different Equations. The fitting of the selected models to the experimental data was evaluated using the coefficient of determination (R^2) and the mean relative percentage deviation modulus ($E\%$) based on Equation (6).

$$E\% = \frac{100}{n} \sum_{i=1}^n \left| \frac{M_{eq} - M'_{eq}}{M_{eq}} \right| \quad (6)$$

where n is the number of data points, M_{eq} denotes the experimental data, and M'_{eq} is the forecast value obtained from the model.

- Guggenheim-Anderson-de Boer (GAB)

$$M_{eq} = \frac{M_0 \times C_g \times k_g \times a_w}{(1 - k_g a_w)(1 + (C_g - 1)k_g a_w)} \quad (7)$$

where M_{eq} is the moisture content ($\text{g} \cdot 100 \text{ g of dry solids}^{-1}$), M_0 is the monolayer value ($\text{g} \cdot 100 \text{ g of dry solids}^{-1}$), a_w is water activity (equilibrium relative humidity $\cdot 100^{-1}$), and C_g and k_g are constants.

- Smith

$$M_{eq} = a - b \ln(1 - a_w) \quad (8)$$

where M_{eq} is the moisture content ($\text{g} \cdot 100 \text{ g of dry solids}^{-1}$), a_w water activity (equilibrium relative humidity $\cdot 100^{-1}$), and a and b are constants.

- Oswin

$$M_{eq} = a \left(\frac{a_w}{1 - a_w} \right)^b \quad (9)$$

where M_{eq} is the moisture content ($\text{g} \cdot 100 \text{ g of dry solids}^{-1}$), a_w water activity (equilibrium relative humidity $\cdot 100^{-1}$), and a and b are constants. Equation (9) can be written in linear form as shown in Equation (10).

$$\ln M_{eq} = \ln a + b \ln \left(\frac{a_w}{1 - a_w} \right) \quad (10)$$

2.3.7. Ash Content and Ash Meting Behavior

In order to estimate ash content, 1–2 g of biomass was placed in the Milestone PYRO microwave muffle furnace at 550 °C for 4 h according to CEN/TS 14775:2004. Then, biomass ash was ground using mortar and moistened with ethanol to make a paste. Next, the paste was pressed into the mold to make a test piece. The ash melting behavior was studied using Hesse Heating Microscope E.M. 201-17K (Hesse Instruments, Osterode am Harz, Germany) based on CEN/TS 15370-1. The sample was heated initially at a rate of 80 °C/min from room temperature to 550 °C. Later the temperature rise is continued at rate of 10 °C $\cdot \text{min}^{-1}$ to the final temperature (i.e., 1750 °C). The camera will record the changes of the sample for every 10 °C start from 400 °C. The camera also records if there the corner angle changes 12%, the shape factor changes 5%, and the area changes 5%.

3. Results

3.1. Influence of Torrefaction on Elemental Composition of Biomass

The elemental composition of both, raw, and torrefied biomass is presented in Table 1. Compared with agricultural wastes i.e., BS (46%) and CS (44%), the wood waste (49%) had higher carbon contents. In contrast to carbon content, agricultural wastes contained more oxygen compared with wood wastes. Among all the selected biomasses, CS had the highest oxygen content i.e., 50.79%.

Table 1. Ultimate analysis of biomass before and after torrefaction treatment.

	C (%)	H (%)	N (%)	S (%)	O (%)	HHV (MJ/kg)
Dried barley straw	45.96	5.30	0.71	0.09	47.94	18.83
225–30 min	46.76	5.52	1.04	0.07	46.61	18.92
275–30 min	52.76	4.88	1.02	0.09	41.25	21.22
300–30 min	56.66	4.32	0.94	0.09	37.99	23.42
225–60 min	47.98	5.10	0.99	0.11	45.82	19.31
275–60 min	53.21	4.73	0.98	0.09	40.98	21.33
300–60 min	61.18	3.81	1.37	0.13	33.51	25.10
Dried cumin stalk	43.74	4.79	0.62	0.05	50.79	18.12
225–30 min	46.30	4.61	0.77	0.07	48.27	19.14
275–30 min	52.15	4.44	0.79	0.11	42.51	21.29
300–30 min	58.66	3.95	0.93	0.07	36.39	24.57
225–60 min	47.98	4.55	0.74	0.06	46.67	19.63
275–60 min	56.23	4.38	0.91	0.06	38.42	23.65
300–60 min	58.00	3.87	1.04	0.12	36.97	24.32
Dried wood wastes	49.03	4.99	0.71	0.03	45.23	19.91
225–30 min	49.79	5.34	0.42	0.04	44.41	20.18
275–30 min	50.78	5.03	0.48	0.02	43.69	22.36
300–30 min	58.41	4.82	0.50	0.02	36.25	23.74
225–60 min	50.78	5.27	0.36	0.03	43.57	20.44
275–60 min	55.08	5.02	0.41	0.02	39.48	22.39
300–60 min	59.66	4.73	0.45	0.02	35.14	24.00

As expected, carbon content of the torrefied biomass increased with increasing torrefaction temperature. For example, when the torrefaction temperature raised from 225 to

300 °C for 30 min residence time, the carbon content increased from 47 to 57% for BS, from 46 to 59% for CS, and from 50 to 58% for WW, respectively.

3.2. Influence of Torrefaction on the Energy Content of Biomass (Heating Value)

The high heating values of raw and torrefied biomasses at varied torrefaction operating conditions are presented in Table 1. In case of raw biomass, the HHV of wood waste i.e., 19.91 MJ·kg⁻¹ was slightly higher than those of agricultural wastes i.e., 18.83 MJ·kg⁻¹ for BS and 18.12 MJ·kg⁻¹ for CS. As expected, the HHV of the torrefied biomass increased with increasing torrefaction temperature. For example, HHV of WW increased from 20 MJ·kg⁻¹ at 225 °C to 24 MJ·kg⁻¹ at 300 °C (for 60 min). From the Table 1, it can be observed that the influence of torrefaction residence time is not very significant on HHV compared with the influence of torrefaction temperature. For example, HHV of BS increased from 18.92 MJ·kg⁻¹ to 19.31 MJ·kg⁻¹ when residence time increased from 30 min to 60 min at 225 °C. On the other hand, for the same biomass i.e., BS, the HHV increased from 19.31 to 25.10 MJ·kg⁻¹ when torrefaction temperature increased from 225 to 300 °C at the same residence time of 60 min.

The variation in atomic ratios of oxygen and hydrogen to carbon i.e., O/C and H/C as presented in van Krevelen diagram (Figure 2). When atomic ratio of O/C reduces, the high heating value of the fuel increases. When torrefaction temperature increased from 225 °C to 300 °C, the O/C ratio reduced from 0.67 to 0.47 for WW, from 0.75 to 0.50 for BS, and from 0.78 to 0.47 for CS.

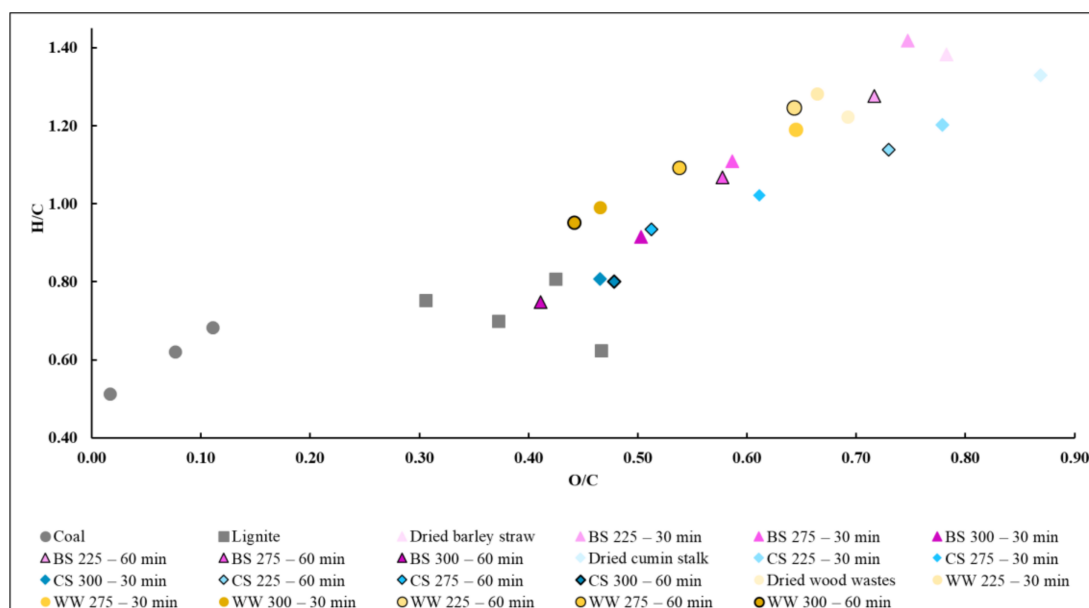


Figure 2. Van Krevelen diagram of dried and torrefied biomass. Coal and lignite data are adopted from Smith and Ross [31].

In contrast to O/C ratio, the high heating value of the fuel reduces with reducing H/C ratio. Torrefaction treatment reduces the hydrogen content in biomass. For example, the H/C ratio reduced from 1.22 to 0.99 for WW, from 1.38 to 0.92 for BS, and from 1.31 to 0.81 for CS, respectively, when biomass was torrefied at 300 °C for 30 min.

3.3. Influence of Torrefaction on Chemical Composition (i.e., Biomass Fibers)

The composition of biomass fiber for both raw and torrefied biomasses are listed in Table 2.

Table 2. Chemical composition of biomass before and after torrefaction treatment.

Biomass/Torrefaction Condition	Cellulose	Hemicellulose	Lignin
Dried barley straw (BS)	41.5 ± 0.5	36.3 ± 0.2	8.8 ± 0.6
TBS 225/30	39.8 ± 0.6	32.4 ± 1.4	10.25 ± 0.07
TBS 275/30	55.6 ± 0.5	2.35 ± 0.10	31.6 ± 0.2
TBS 300/30	30.8 ± 0.7	3.7 ± 0.9	30.00 ± 0.14
TBS 225/60	42.18 ± 0.18	28.33 ± 0.05	12.3 ± 1.0
TBS 275/60	48 ± 2	2.6 ± 0.5	33 ± 3
TBS 300/60	5.5 ± 0.7	5.00 ± 0.10	48.2 ± 0.3
Dried cumin stalk (CS)	44.0 ± 0.7	11.3 ± 0.8	10.86 ± 0.04
TCS 225/30	38.8 ± 0.2	11.3 ± 0.6	17.3 ± 0.4
TCS 275/30	24 ± 2	5.0 ± 0.7	34.1 ± 0.5
TCS 300/30	10.4 ± 0.8	6.28 ± 0.13	36.40 ± 0.01
TCS 225/60	39.76 ± 0.07	6.86 ± 0.17	18.2 ± 0.9
TCS 275/60	18.1 ± 1.0	4.51 ± 0.04	33.40 ± 1.1
TCS 300/60	9.26 ± 0.01	4.31 ± 0.01	35.30 ± 0.01
Dried wood wastes (WW)	53.5 ± 0.7	16.0 ± 0.7	20.60 ± 0.14
TWW 225/30	49.4 ± 1.6	15.43 ± 0.03	20.70 ± 0.14
TWW 275/30	46.5 ± 1.2	3.4 ± 1.2	35.50 ± 0.01
TWW 300/30	34.71 ± 0.10	4.58 ± 0.07	48.7 ± 0.9
TWW 225/60	43.3 ± 0.6	14.12 ± 0.10	25.3 ± 1.1
TWW 275/60	46.63 ± 0.01	5.2 ± 1.0	38.3 ± 0.10
TWW 300/60	30.5 ± 0.9	5.1 ± 1.0	55.9 ± 0.4

As expected, among the selected biomasses, WW had the highest lignin content i.e., 20.6% compared with agricultural wastes BS (8.8%) and CS (10.86%). At the same time, BS (36%) contained more hemicellulose compared with CS (11%) and WW (16%). As the hemicellulose content reduced significantly, the cellulose and lignin content increased, relatively. From the Table 2, it can be observed that cellulose content increased from 41.5% to 48% in case of BS torrefaction at 275 °C for 60 min. In contrast to cellulose and hemicellulose, the lignin content increased with increasing torrefaction temperature. The lignin content increased from 8.8% to 48.2% for BS, from 10.86% to 35.30% for CS, and from 20.60% to 55.9% when biomass was torrefied at 300 °C for 60 min.

3.4. Moisture Uptake and Moisture Adsorption

The moisture uptake of both raw and torrefied biomass after 3 days of storage at 30 °C with RH 95% are presented in Table 3. A comparative analysis shows that moisture uptake was higher in case of agricultural wastes compared with WW in both the cases i.e., raw biomass and torrefied biomass. The moisture uptake for raw agricultural waste were higher than 22%, while for raw wood waste only 18%. As a general trend, the moisture uptake reduced with increasing torrefaction temperature. For example, the absorbed moisture was 18.29% for raw WW and 8.46% for WW torrefied at 300 °C for 30 min. The moisture uptake of torrefied biomass produced at 300 °C and 30 min was 13%, 22%, and 8% for BS, CS, and WW, respectively. Among the agricultural wastes, CS showed higher moisture uptake for all the torrefaction conditions studied.

Table 3. Moisture content (wt.%) and moisture uptake (%) of raw and torrefied biomasses.

Biomass	MC (%)	Moisture Uptake (%)
Dried barley straw (BS)	8.73 ± 0.19	22.75 ± 0.16
TBS 225/30	5.39 ± 0.15	19.0 ± 0.3
TBS 275/30	4.3 ± 0.4	13.45 ± 0.03
TBS 300/30	3.91 ± 0.13	12.96 ± 0.13
TBS 225/60	5.2 ± 0.2	18.28 ± 0.05
TBS 275/60	5.34 ± 0.16	12.9 ± 0.3
TBS 300/60	4.46 ± 0.19	14.5 ± 0.8
Dried cumin stalk (CS)	9.42 ± 0.07	24.6 ± 0.3
TCS 225/30	2.58 ± 0.17	22.0 ± 0.2
TCS 275/30	3.48 ± 0.18	20.1 ± 0.4
TCS 300/30	5.23 ± 0.16	22.12 ± 0.04
TCS 225/60	2.77 ± 0.15	19.34 ± 0.04
TCS 275/60	3.34 ± 0.17	19.45 ± 0.02
TCS 300/60	3.89 ± 0.17	20.71 ± 0.13
Dried wood waste (WW)	8.871 ± 0.001	18.29 ± 0.12
TWW 225/30	1.58 ± 0.17	13.9 ± 0.3
TWW 275/30	1.6 ± 0.7	8.99 ± 0.14
TWW 300/30	1.9 ± 0.4	8.46 ± 0.04
TWW 225/60	1.86 ± 0.11	11.53 ± 0.10
TWW 275/60	1.886 ± 0.004	8.61 ± 0.01
TWW 300/60	2.36 ± 0.02	8.35 ± 0.13

In Table 4, equilibrium moisture content at various equilibrium relative humidity (ERH) for raw biomass and torrefied biomass at 300 °C for 60 min are presented. Results indicate that the higher the ERH, the higher the equilibrium moisture content (EMC) for all biomass. At the lower ERH, the EMC of raw and torrefied biomass was no discernible difference.

Table 4. Equilibrium moisture content (%) of raw and torrefied biomass at 300 °C for 60 min.

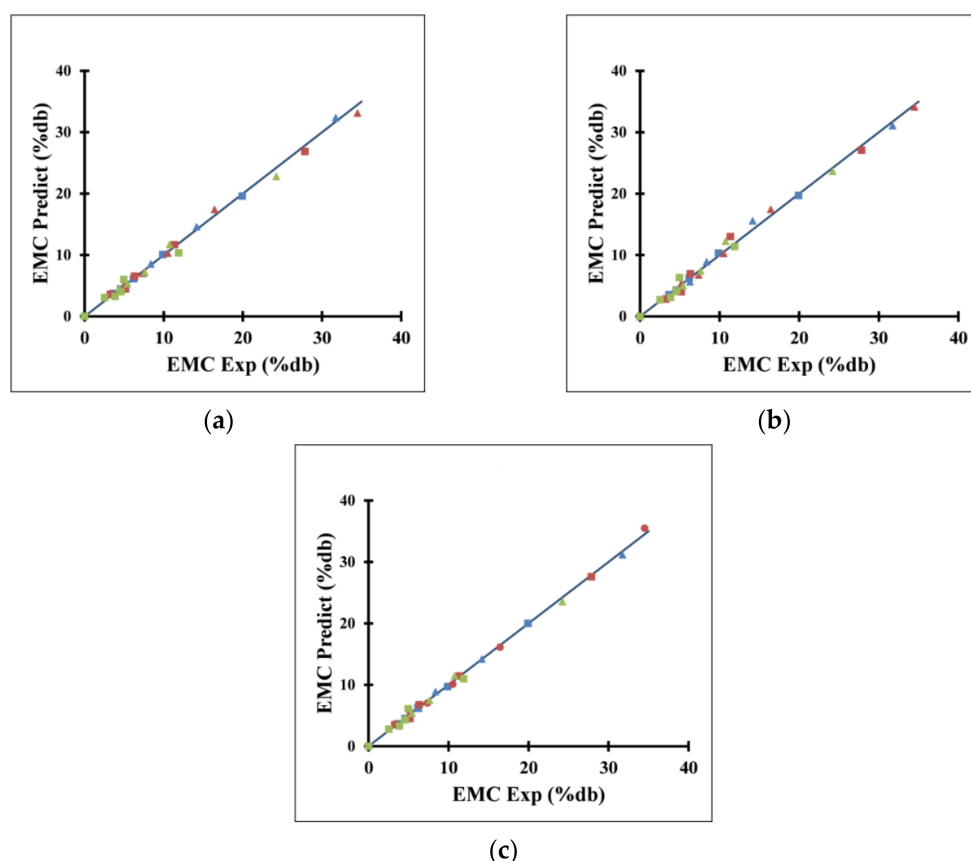
ERH (%)	Equilibrium Moisture Content (% db)					
	BS	TBS	CS	TCS	WW	TWW
95	31.7 ± 0.3	19.9 ± 1.1	34.5 ± 0.4	27.85 ± 0.12	24.22 ± 0.14	11.88 ± 0.15
75	14.2 ± 0.2	9.87 ± 0.10	16.4 ± 0.4	11.4 ± 0.3	10.8 ± 1.1	4.95 ± 0.01
50	8.36 ± 0.12	6.17 ± 0.02	10.5 ± 0.3	6.32 ± 0.06	7.62 ± 0.08	4.59 ± 0.05
30	6.28 ± 0.15	4.55 ± 0.16	7.36 ± 0.15	5.17 ± 0.01	5.41 ± 0.09	3.9 ± 0.4
20	5.05 ± 0.03	3.65 ± 0.11	5.18 ± 0.12	3.26 ± 0.04	4.37 ± 0.08	2.53 ± 0.04

The more significant difference of EMC was observed at higher ERH. For example, the EMC values of 5.05% and 3.65% was observed for raw BS and torrefied BS at ERH of 20%, while the EMC values of 31.7% and 19.9% was observed for raw BS and torrefied BS at ERH of 95%. The highest EMC for each ERH was in raw CS, while the lowest EMC was in the torrefied WW.

Three mathematical models were used to fit the experimental data. The moisture adsorption parameters are presented in Table 5. A comparative analysis between experimental EMC and calculated EMC values are presented in Figure 3.

Table 5. Moisture adsorption parameter for raw and torrefied biomass.

Biomass	GAB					Smith				Oswin			
	M_0	C_g	k_g	R^2	$E\%$	a	b	R^2	$E\%$	a	b	R^2	$E\%$
BS	4.84	41.16	0.90	0.9932	2.62	2.22	9.63	0.9925	8.40	8.87	0.43	0.9977	2.49
TBS	3.68	25.15	0.86	0.9908	1.80	2.23	5.84	0.9981	3.17	6.30	0.39	0.9996	1.04
CS	6.80	9.81	0.84	0.9309	4.42	3.06	10.37	0.9971	4.33	10.10	0.43	0.9951	4.20
TCS	3.93	13.60	0.90	0.8865	6.68	0.90	8.74	0.9868	12.47	6.77	0.48	0.9898	5.70
WW	4.22	40.57	0.86	0.9094	5.37	2.49	7.06	0.9885	6.83	7.46	0.39	0.9970	2.57
TWW	2.31	−49.58	0.82	0.6269	16.85	2.02	3.12	0.9452	13.46	4.31	0.32	0.9319	12.26

**Figure 3.** Comparison of equilibrium moisture content (EMC) from experimental and EMC prediction for each model (a) GAB, (b) Smith, and (c) Oswin.

From the Table 5 and Figure 3, it can be observed that, for both raw and torrefied barley straw, the models GAB and Oswin are well fitted. For the raw and torrefied cumin stalk, Oswin is the best model. For the raw wood waste, the best fit model is Oswin. For the torrefied wood waste, the mean relative percentage deviation modulus of the three models is higher than 10% which indicates that the models are not a good fit for practical purpose. The GAB model can be used to predict the monolayer moisture content (M_0). From the Table 5, it can be observed that M_0 values are reduced for torrefied biomass compared with raw biomass. For example, the calculated M_0 values are 4.84% and 3.68% for raw and torrefied BS at 300 °C. This could be attributed to the increased cellulose crystallinity during torrefaction. According to Yao et al., [32], the monolayer moisture content decreases with increasing cellulose crystallinity.

The moisture adsorption isotherm curve of experimental and predicted data from Oswin model for both dried and torrefied biomass is presented in Figure 4.

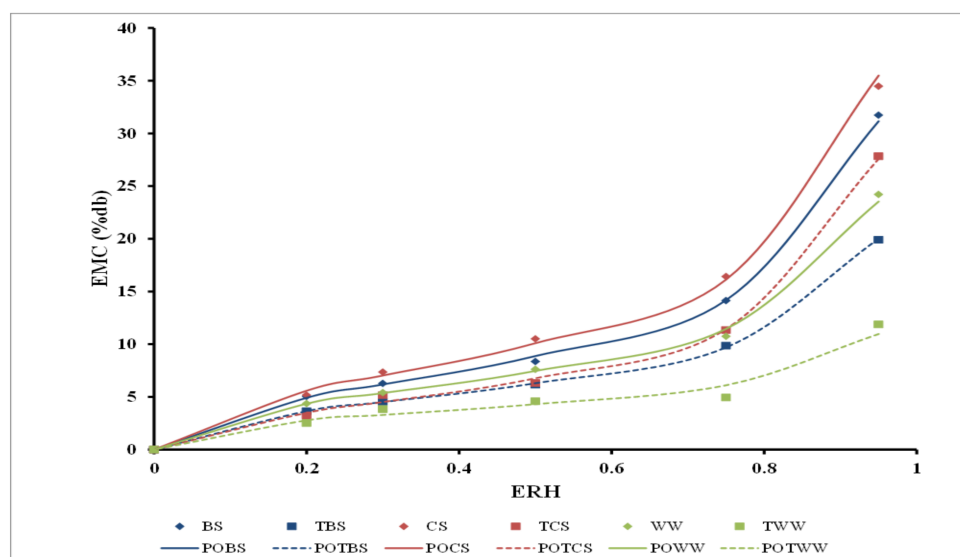


Figure 4. Experimental result and isotherms predicted by Oswin (PO) model for raw and torrefied biomass.

3.5. Ash Content and Ash Melting Behavior

From Table 6, it can be observed that ash content in raw agricultural waste was higher than in wood waste.

Table 6. Ash content of raw biomass and biomass torrefied at different temperatures with 60 min of residence time.

Biomass	Ash Content (%)
Dried barley straw (BS)	3.5 ± 0.2
TBS 225	4.8 ± 0.4
TBS 275	6.15 ± 0.10
TBS 300	9.51 ± 0.09
Dried cumin stalk (CS)	6.86 ± 0.14
TCS 225	7.0 ± 0.3
TCS 275	10.2 ± 0.3
TCS 300	13.00 ± 0.2
Dried wood waste (WW)	0.77 ± 0.06
TWW 225	1.34 ± 0.17
TWW 275	1.79 ± 0.08
TWW 300	2.09 ± 0.18

The influence of torrefaction on the ash melting behavior during combustion was studied by characterizing the ash melting temperatures. The Figure 5 shows the ash melting temperatures i.e., initial deformation temperature (IDT), sphere temperature (ST), hemisphere temperature (HT) and flow temperature (FT) for both raw and torrefied (at 300 °C and 60 min) biomass. In this study, the initial deformation temperatures were in the order of $CS < BS < WW$. The observed IDT values for raw biomass are 620 °C, 590 °C, and 1147 °C for BS, CS, and WW, respectively. Interestingly, the HT and FT for CS and WW are in the similar range i.e., 1500–1550 °C. The same temperatures for straw are much lower i.e., 1053 °C and 1057 °C for HT and FT, respectively.

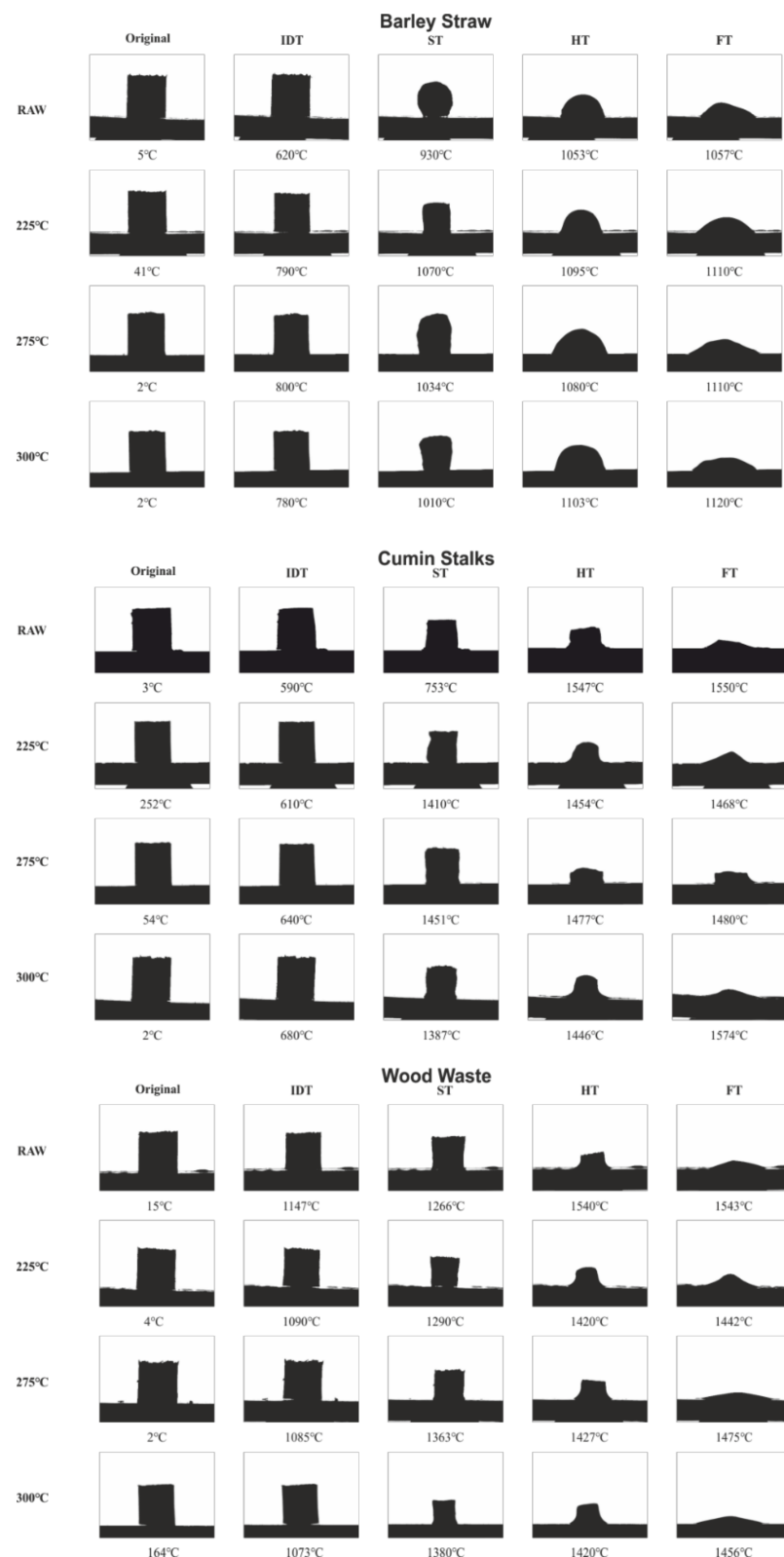


Figure 5. Ash melting temperatures of raw and torrefied biomass.

From Figure 5, it can be observed that torrefaction treatment had a significant effect on all the ash melting temperatures. The first observation is the common trend of increasing IDT values for BS and CS with increasing torrefaction treatment. In contrast, a downward trend of IDT values with increasing torrefaction temperature was observed for WW. For example, the IDT values increased from 620 °C to 790 °C, 800 °C, and 780 °C for torrefaction

temperatures 225 °C, 275 °C, and 300 °C, respectively. However, it is worth to note that the IDT values for torrefaction temperature of 300 °C was slightly reduced compared with 275 °C in case of BS and WW.

4. Discussion

4.1. Influence of Torrefaction on Elemental Composition of Biomass

After torrefaction the change of carbon content in WW was lower than in BS and CS. The reason could be the higher oxygen and hydrogen contents of BS and CS. As torrefaction temperature increases, relatively higher amount of hydrogen and oxygen reduces compared with carbon because of the dehydration and depolymerization of biomass components during torrefaction [11,33]. Previous studies on biomass torrefaction also observed the similar trend of increasing carbon content and reduced hydrogen and oxygen contents in the torrefied biomass compared with raw biomass. For example, Manatura et al. [14] reported increase in carbon content from 46% to 58% when sugarcane bagasse was torrefied at 275 °C. At same torrefaction temperature, the authors also observed reduction of hydrogen and oxygen contents from 6% to 3% and 46% to 38%, respectively. In another study, Singh et al. [34] observed a rise of around 10% in carbon content when pigeon pea stalk was torrefied at 300 °C for 30 min.

4.2. Influence of Torrefaction on the Energy Content of Biomass (Heating Value)

The changes in the high heating values are mainly because of the loss of oxygen content and relative increase in the carbon content. Although hydrogen content is reduced during the torrefaction, its influence on high heating value is not very significant. At the same time, the relative loss of oxygen is higher compared with hydrogen loss during torrefaction. From the van Krevelen diagram (Figure 2), it can be observed that the properties of torrefied biomass are moving towards coal with increasing torrefaction temperature and residence time. Solid fuel with low H/C and O/C ratios is more accepted as a fuel because it indicates low energy loss and less smoke during combustion [35]. The variation in the high heating values and atomic ratios i.e., O/C and H/C observed in this study during torrefaction followed the same trend of previously published data [11,27,36]. For example, Wang et al. [11] reported an increase of HHV from 19.75 MJ·kg⁻¹ to 23.61 MJ·kg⁻¹ when Norwegian spruce stem wood was torrefied at 300 °C for 60 min. In another study, Chen et al. [36] reported a reduced O/C ratio from 0.66 to 0.35 when sawdust was torrefied at 270 °C for 60 min.

4.3. Influence of Torrefaction on Chemical Composition (i.e., Biomass Fibers)

The hemicellulose content in torrefied biomass is lower than that in raw biomass. After torrefaction at 275 °C during 60 min, the hemicellulose in barley straw decreased by more than 90%, while in cumin stalk it decreased by 60% and wood waste by 68%. This result is in line with previous studies [37–39]. The composition of hemicellulose is different for each biomass, causing the thermal degradation of hemicellulose for each biomass also different. Xylan is the most unstable component of hemicellulose. The xylan content in barley straw ranges from 20% [40] while in wood waste with softwood as the main component has 5–10% xylan content [41]. High xylan content causes the degradation in barley straw is higher than in wood waste. Reduced levels of hemicellulose, the most reactive fiber, are expected in biomass heated at 220–315 °C. According to Yang et al. [42], at this temperature hemicellulose undergoes thermal degradation.

The significant reduction in cellulose content was observed for both agricultural wastes. For example, for BS the cellulose content reduced from 48% to 5.5% when biomass torrefaction temperature increased from 275 °C to 300 °C for 60 min residence time. However, different results were observed in case of WW, where cellulose content was only reduced from 47% to 31%. According to Barta-Rajnai et al. [37], the reason for the increased degradation of cellulose in case of agricultural waste could be attributed to the catalytic effect of ash. The agricultural biomass contains more ash compared with WW. The ash

content of BS, CS, and WW were 3.5 wt%, 6.86 wt%, and 0.77 wt%, respectively. Previously, Barta-Rajnai et al. [37] observed the increased degradation of cellulose during herbaceous biomass torrefaction at 300 °C.

The thermal degradation of cellulose is also influenced by the crystallinity of cellulose. Crystallinity of barley straw was 38% [43] while softwood was higher than 53% [44]. Cellulose with low crystallinity has low thermal stability due to its tendency to accelerate in the degradation process [45]. In another study, Chen et al. [38] also observed 77% of cellulose degradation from its original content when dried rice husk is torrefied at 290 °C for 30 min.

The lignin content in torrefied biomass is higher than that in raw biomass. It is worth to note that lignin presented in this study is a representative of ash-free acid insoluble portion of the biomass. According to Barta-Rajnai et al. [37] and Shoulaifar et al. [39], this acid insoluble portion of the torrefied biomass may also contain acid insoluble compounds other than lignin, which are mainly produced during the cellulose degradation. Other authors also observed the same trend of increasing lignin with increasing torrefaction temperature. For example, Singh et al. [46] also observed the rise in lignin content from 24.2% to 59.9% during the torrefaction of *A. nilotica* at 300 °C. Chen et al. [38] reported, an increased lignin content from 14% to 62% for rice husk torrefaction at 290 °C. In another study, Shoulaifar et al. [39] observed acid insoluble lignin content of 175.5 mg·g⁻¹ of biomass for raw birch wood and 260.7 mg·g⁻¹ of biomass for same birch wood torrefied at 255 °C.

4.4. Moisture Uptake and Moisture Adsorption

The main reason for the reduced moisture uptake in case of torrefied biomass is the breakdown of the hydroxyl and carboxyl groups present in hemicellulose and amorphous region, which form hydrogen bonds with water [47]. The increased crystallinity of the biomass during torrefaction also limits the absorption of moisture [48].

However, the moisture adsorption capacity of the torrefied biomass could also be related with other parameters such as ash content, and porosity. Torrefaction treatment increases biomass porosity because of the degradation of biomass components. Previously, Chen et al. [49] observed that the surface area increased from 73.6 m²·g⁻¹ and 99.9 m²·g⁻¹ to 159.9 m²·g⁻¹ and 170.0 m²·g⁻¹ when raw cotton and corn stalks are torrefied at 290 °C respectively. At the same time, the ash present in biomass can accelerate the degradation of biomass components because of its catalytic effect and thereby increase the porosity during thermal treatment. Previous studies reported that, porosity in pyrolytic carbon is significantly affected by inorganic elements especially magnesium, potassium, and sulphur [50]. Interestingly, the moisture uptake of the torrefied biomass followed the same order of ash content in selected biomass i.e., CS > BS > WW.

Another parameter that affects the water adsorption capacity is cellulose crystallinity. The hemicellulose and amorphous cellulose absorbs more water than crystalline cellulose [48,51]. As the torrefaction temperature increases the hemicellulose and amorphous cellulose fractions degrades and the crystallinity of the cellulose increases [52]. According to Hill et al. [53], at low temperature torrefaction, the molecules on the solid surface consisting of crystals undergo conformation to form a relatively hydrophobic surface. This phenomenon could be the reason for the increased hydrophobicity of the biomass with increasing torrefaction temperature. However, at higher torrefaction temperature i.e., >275 °C the crystallinity of the cellulose reduces. At high temperatures, torrefaction causes a decrease in the lateral crystal dimensions, interior crystal chain proportions and the crystallinity index. This forms a layer that tends to be more hydrophilic [53].

Similar results for moisture uptake have been observed in case of mixed wood waste torrefied biomass. Previously, Peng et al. [54] observed a moisture uptake of around 9% for wood waste torrefied at 300 °C for 60 min and the climate chamber conditions of 90% RH and 30 °C.

The shape of moisture adsorption isotherm curve for raw and torrefied biomass is sigmoidal. This shape represents type II isotherm based on the BET classification. Previously, this type of isotherm has also been shown to fit for both raw and torrefied corn stover [55] and also for other biomass such as pine, spruce, birch, and willow [56]. Type II relates to the adsorption process in the form of a monolayer, followed by formation of the next layer as a result of increased vapor pressure [57]. This type of isotherm curve can be divided into three parts. The first is concave down at low RH, the second is the horizontal in the middle of the curve, and the third is the upward concave at high RH. Each section in the isotherm indicates a different type of water bond. The first part is often called the water monolayer which is formed from the bonds of water molecules with the plant fibers, especially the amorphous part [55]. The polar ends of water molecules in the monolayer bind to the next layer of water which is called the secondary bonded water layer [58]. In areas above the monolayer, water molecules are trapped in new pores that are formed from the swollen structure [59].

4.5. Ash Content and Ash Melting Behavior

After torrefaction, the ash content was increased. The ash content in the torrefied biomass followed the increasing order with increasing torrefaction temperature i.e., the higher the torrefaction temperature, the higher the ash content. The ash content of any biomass torrefied at 300 °C was more than twice the value that of raw biomass. This result is in line with previous research [60,61]. During the torrefaction, while the organic matter degrades, the inorganic compounds are not decomposed, which leads to an increased concentration of ash [62].

IDT of agricultural waste was lower than wood waste. Niu et al. [63] observed low IDT values i.e., 591 °C and 631 °C for cotton stalks ash produced at 400 °C and 600 °C (ashing temperatures). The similar values of IDT i.e., 1190 °C and 1160 °C, were reported for pine and eucalyptus biomass [64]. In the literature researchers considered different ash melting temperatures i.e., IDT, ST, and HT in order to differentiate the range of slagging and fouling tendency as low, medium, and high. Previously it has been established that herbaceous biomass possesses high risk of ash sintering compared with woody biomass [65]. For example, Wang et al. [66] presented the degree of ash fouling based on ST values as light (>1390 °C), medium (1260–1390 °C) and serious (<1260 °C). According to this classification, the crop residues BS and CS were in the serious fouling range and wood waste in the medium fouling range. Torrefaction temperature increased the softening temperature for all the biomass samples studied. Especially, for CS interesting results were observed. The ST values were increased from 753 °C for raw CS to 1451 °C for torrefaction temperature 275 °C. As a result of this increased softening temperature the fouling tendency of CS's ash is shifted from serious range to low range. On the other hand, the downward trend of ST values was observed in the case of torrefaction temperature 300 °C compared with 225 °C and 275 °C. Previously, Wang et al. [66] also observed reducing ST values with increasing thermal treatment temperatures. The authors observed that, the softening temperature of maize straw char briquetting reduced from 1081 °C to 1050 and 1039 °C when pyrolysis temperature increased from 250 °C to 350 °C and 450 °C, respectively. Coming to HT and FT values, a mixed trend was observed. For BS, the HT and FT values were in the increasing order with increasing torrefaction temperature. In contrast, the HT and FT values were reduced with increasing torrefaction temperatures in case of CS and WW.

From the above discussion, it can be observed that torrefaction treatment showed significant influence on the melting behavior of the biomass ash. This could be attributed to the changes in the chemical composition of the ash. The biomass ash contains different types of components and in that chlorine (Cl), potassium (K), sodium (Na), and silica (Si), etc. are mainly responsible for the ash-related issues in the biomass thermal conversion. The melting point of silica (i.e., 1710 °C) is higher than the common operating temperature of biomass thermal conversion processes. However, silica reacting with potassium and sodium forms low-melting temperature eutectics [67]. Chlorine plays a critical role in the

ash fusibility, as it reacts with alkalis (K and Na) and produces low eutectic temperature compounds, such as KCl and NaCl (melting temperatures are 770 °C and 801 °C) [67]. The biomass, such as straws and grasses are known for their high amount of silica and chlorine. In addition, potassium also plays a critical role in the slagging and agglomeration by forming low melting temperature compounds, such as K₂SO₄.

The previous studies showed that the torrefaction treatment reduced the Cl and K content of the biomass. Keipi et al. [68] reported that torrefaction treatment reduced the elemental chlorine up to 90% compared with raw eucalyptus biomass. In the recent study, Sá et al. [69] observed complete removal of chlorine during the torrefaction of eucalyptus biomass. In another study Saleh et al. [70], the influence of torrefaction treatment on the chlorine content of straw, *Miscanthus*, spruce, and polar biomass. The authors reported that the chlorine released is increased from 20% to 70% when torrefaction temperature increased from 250 °C to 350 °C. A study on the release of chlorine and potassium during the torrefaction of wheat straw reported that around 15.37% of potassium was released during the torrefaction at 300 °C. Liu et al. [71] reported release of 9.1% sodium during the torrefaction of food waste at 300 °C. Based on this discussion, the increased initial deformation and softening temperatures of biomass ashes with torrefaction treatment could be linked to the release of chlorine and potassium and changes in the concentration of other elements. However, a detailed ash composition analysis is further needed to better understand the influence of torrefaction treatment on the ash melting characteristics of the biomass. This will be the topic of our future study.

5. Conclusions

Torrefaction has significant influence on hemicellulose content in the biomass, but less on cellulose and lignin contents. Torrefaction pretreatment increased the carbon content in the range of 0.8–15.22% and reduced oxygen content in the range of 0.82–14.43% depending on torrefaction temperature. There was also an increase of heating value with increase of torrefaction temperature. The highest heating value in this study was measured in torrefied barley straw at 300 °C for 60 min. Torrefied biomass showed hydrophobic properties with lower moisture uptake in the range of 8.35–22.12%. Further moisture adsorption isotherm curve follows type II isotherm based on the BET classification and indicates the multilayer of water adsorption. The best model to describe the moisture adsorption isotherm was the Oswin model. Torrefaction had a positive influence on ash melting behavior of the biomass thus, reducing the fouling tendency of agricultural waste. Overall, this study shows that torrefaction influences the fuel properties of biomass by increasing the heating value, decreasing the moisture content and moisture uptake, and reducing fouling tendency. Based on this research, the torrefaction seems to be a promising pretreatment for further applications of biomass such as co-combustion with other solid fuel.

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