Hydrothermal conversion of different lignocellulosic biomass feedstocks – Effect of the process conditions on hydrochar structures

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Abstract

Five biomass feedstocks (Coffee residues, Rice waste, Whitewood, Zilkha black, and Lignin) were hydrothermally processed in a semi-continuous flow rig using 9 different processing conditions (75, 150, 250 ºC, and 1, 50, 240 bar). Solid residues produced at low temperature (<150 °C) did not show significant structural changes. At more severe conditions, structural changes could be linked to the lignocellulosic composition and divided into three categories: (i) biomass with higher hemicellulose-cellulose and lower cellulose-lignin structures, (ii) lower hemicellulose-cellulose and higher cellulose-lignin structures, and (iii) only cellulose-lignin structures. Both hemicellulose and cellulose structures in category (i) and (ii) were successfully degraded under subcritical conditions (250 °C and 50 bar) to produce hydrochar with higher lignin content. Biomasses with higher levels of lignin did not show the same degree of transformation. Category (i) produced a low hydrochar yield (39 wt.%) due to the degradation of higher hemicellulose-cellulose structures. Category (ii) had higher hydrochar yields (58-62 wt.%) due to the lower amount of cellulose and hemicellulose. Category (iii) had the highest hydrochar yields (73-90 wt.%) thanks to the lack of hemicellulose and lower cellulosic structures. A novel concept called “displacement”, based on a thermogravimetric profiling method, was used to quantify changes in the pyrolysis behaviour of the hydrochar compared to the original feedstock. The degree of “displacement” correlated with hydrochar yield and reactivity, the highest level of displacement was observed with category (i- higher hemicellulose-cellulose biomasses) while the lowest displacement was observed with category (iii- higher lignin biomasses). This novel technique could be used to quantify the effects of hydrothermal treatment on any given biomass.

Keywords: Hydrothermal conversion, Hydrochar, Bioenergy, Lignocellulosic Biomass, Displacement.

1 Introduction

Thermal and biological biomass processing technologies such as pyrolysis, combustion, hydrothermal processes (liquefaction, gasification, and carbonisation) and biochemical conversion have all been identified as pathways to decrease CO_2 emissions and reach the 2 °C climate target [1]. Biomass is defined as inexpensive, clean, and environmentally friendly energy sources [2, 3] and an integral part of the global carbon cycle [4]. However, there are several obstacles to the full commercialisation of bioenergy and bioproducts via these technologies, which include the resourcing of biomass, inadequate biomass refinery technologies, a lack of cost-competitive bioproducts and a limited and/or unstable supply of biofuels and bioproducts [5]. Furthermore, the chemical and biological variations in different types of biomass can result in significant changes in characteristics (grinding, handling, composition etc) that can hinder the commercialisation of these technologies[6-8]. Lignocellulosic biomass feedstocks are defined as one of the crucial renewable energy sources thanks to its availability, high energy content, and reactivity. The lignocellulosic biomass chars can be produced by pyrolysis, torrefaction, and hydrothermal processes [9]. The lignocellulosic biomasses are composed of hemicellulose, cellulose, and lignin in addition to a small quantity of extractives and ashes [10]. Although the composition of lignocellulosic biomass varies according to the type, location, maturity, and climate conditions, on average it consists of about 15-30% of hemicellulose, 40-60% of cellulose, and 10-25% of lignin [11].

Hydrothermal processing is one of the most promising technologies, as it can use the high inherent moisture of biomass to its advantage [12]. For other processing techniques, such as pyrolysis and combustion, the high moisture content needs to be removed which requires a significant amount of energy for drying processes. In contrast, hydrothermal conversion of biomass in hot-compressed water is a viable, scalable, and energy-efficient thermo-chemical route for converting biomass into a synthetic solid, liquid, or gaseous fuels and chemicals [13]. In hydrothermal treatments, water can be a solvent, a reactant and/or a catalyst in the hydrolysis reactions. The process also leads to by-products that can be used for power generation and the recovery of useful nutrients [14]. In this process, the biomass conversion is carried out by several complex reactions depending on the physical properties of the water, which are usually manipulated changing the temperature, pressure, and contact time of the water-biomass in order to obtain the desired products. The hydrothermal conversion is therefore classified into three

processes namely carbonisation, liquefaction and gasification depending on the severity of the operating conditions [15-18].

Hydrothermal gasification (HTG, >350 ºC) is carried out near-critical or above-critical conditions to produce a synthetic fuel gas (syngas), which is rich in CH_4, H_2, CO_2, and CO depending on experimental conditions [15]. Depending on the biomass, the syngas may contain a significant amount of undesirable impurities such as sulphur compounds (SO_2), nitrogen compounds (NH_3 and HCN), hydrogen halides (HCI and HF) [16]. Hydrothermal liquefaction (HTL, 250-370 ºC, 50-240 bar) is the wet processing route for high moisture biomasses to produce of a liquid fuel (bio-crude) [15], which is similar to petroleum crude and can be upgraded to a range of petroleum-derived fuel products [17]. Since HTL involves the direct conversion of the biomass into bio-crude in the presence of a solvent, it eliminates the high drying costs [18-20]. Hydrothermal carbonization (HTC, 180-250 ºC, 15-40 bar) is a thermochemical process for the pre-treatment of high moisture content biomass to make it viable in for energy production [17, 21, 22]. HTC uses relatively low temperatures and is suitable for any kind of biomass feedstock [23]. HTC can convert lignocellulosic materials into solid hydrochar, which have better physicochemical characteristics than raw biomass feedstocks [24], and also produce liquid products that contain organic and inorganic value-added chemicals [25]. The HTC hydrochars exhibits lower O/C and H/C ratios compared to dry torrefaction and turn into more lignin or coal type materials [26]. HTC hydrochars can be used in a wide range of processes such as soil amendment [27], CO_2 capture [28], nanoparticles (for making composites) [29], energy production [30], water purification [31] thanks to their physicochemical properties [32]. Although the lab-scale research on HTC of various biomass feedstocks has been recently progressed and provided significantly promising results, the HTC process needs further investigations in terms of process and reactor types, biomass feedstocks, and conditions due to the complex reaction mechanisms and operational barriers to make this technology as a commercial technology [25]. For example, a continuous HTC process would be one of the key components for a potential industrial application of HTC, as most HTC research have been carried out in batch [25].

In this study, the hydrothermal conversion of five different lignocellulosic biomass feedstocks (Coffee residues, Whitewood, Rice waste, Zilkha black, and Lignin) was investigated in a semi-continuous process at different temperatures (75, 150, and 250 ºC) and pressures (1, 50 and 240

bar) to produce hydrochars. Each hydrochar sample was characterised in a Thermogravimetric Analyser (TGA) using a slow pyrolysis methodology to identify the effects of hydrothermal treatments on hydrochar structures using thermal decomposition behaviours. Additionally, a new method called "displacement" was shown to provide quantitative information about the impact of hydrothermal treatment on the lignocellulosic composition of biomass feedstocks. This method has been previously used as a fingerprint technique for biomass identification as it can quantify hemicellulose, cellulose and lignin levels present in any type of biomass [33].

2 Material and Methods

The effects of the hydrothermal conversion process conditions on the hydrochar structures were investigated using five different biomass feedstocks namely Coffee residues (CR, as an industrial waste, obtained from spent aluminum capsules used in certain domestic coffee machines), Whitewood (WW, as a forest waste, obtained from sawdust of white wood), Rice waste (RW, as a food waste, obtained from rice pellets), and Zilkha black (steam exploded white wood pellets) and Lignin (ZB and LG as high carbon ratio materials, obtained from Zilkha Black® pellets and Lignin pellets). These feedstocks have been selected due to their abundance in environment and commercial availability, as well as their potential to produce hydrochars having different properties [6, 34, 35]. Zilkha was chosen as it represents a wood based, lignocellulosic feedstock but one that has already been pretreated/upgraded using thermal methods. The biomass feedstocks (CR, WW, RW, ZB and LG) were firstly ground into a powder and sieved in particle sizes of 200-1000 μm in a sieve shaker for 15 minutes using the standard method of EN ISO 17827-2:2016 – *Solid biofuels – Determination of particle size distribution for uncompressed fuels – Part 2: Vibrating screen method using sieves with aperture of 3,15 mm and below* [36, 37].

2.1. Hydrothermal processing

The biomass feedstocks (CR, WW, RW, ZB, and LG) were hydrothermally processed using a semi-continuous flow rig shown in Figure 1. The operation of the rig consists of a semi-continuous reactor that works by preloading a biomass sample inside a 100 micron mesh and processing using a semi-continuous hydrothermal flow. The feed stream (distilled water) TK-101 is pumped using a high pressure Gilson HPLC pump (P-101) and preheated to the desired temperature using a Watlow cartridge heater (E-101). The preheated water stream flows into the reactor (R-101) from the bottom, where the reaction starts with the effects of matter and

energy transfer. The enriched stream leaves the reactor and passes through a filter (F-101) of 100 µm that retains any solids that could potentially have flowed out the top of the reactor. After the filter, the resulting products are cooled in a heat exchanger (E-102) with a stream of fresh water. Finally, the product stream goes through a back-pressure regulator (BPR) which pressurizes the whole system and the outflow is collected after the BPR (TK-102). The main focus of this study was the residual solids in the reactor rather than the contents of the liquid effluent.

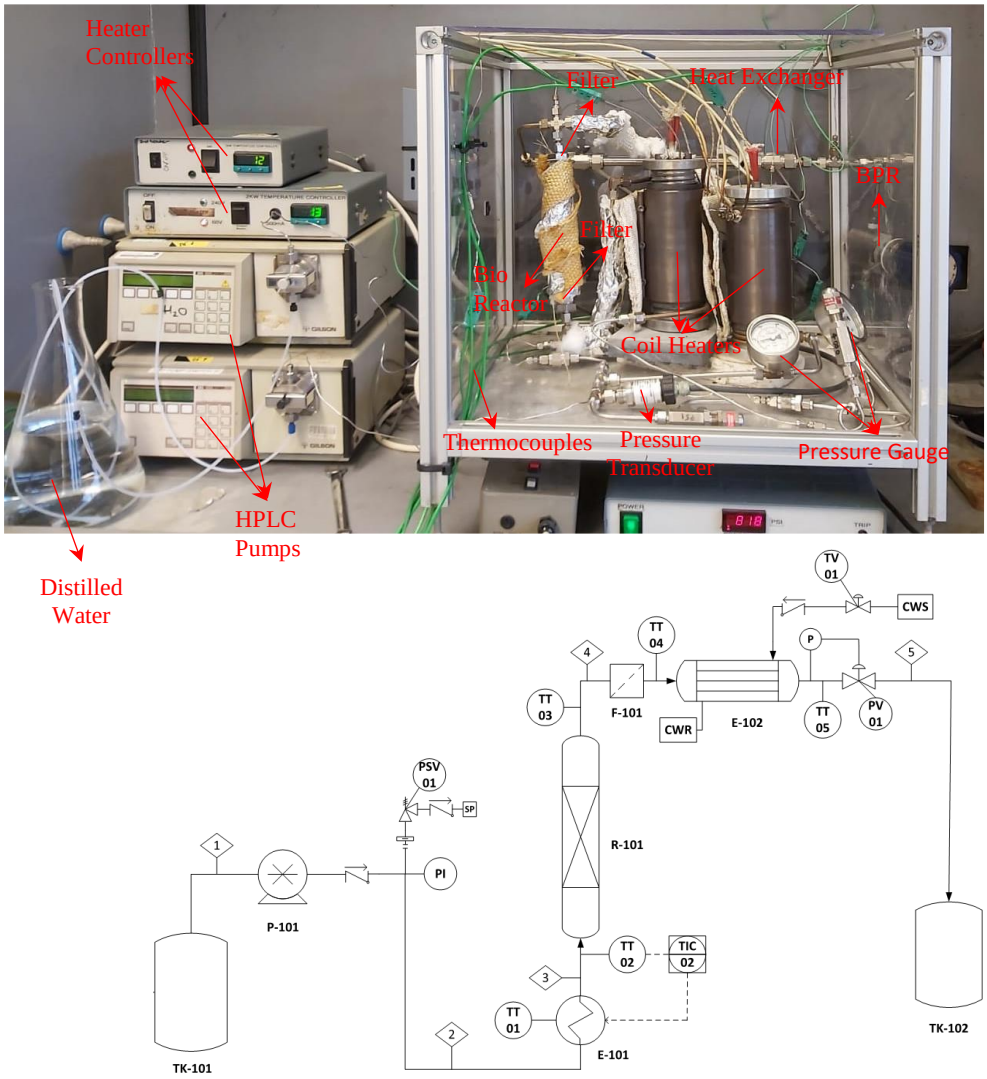


Figure 1. Semi-continuous hydrothermal treatment process rig and flow diagram.

The hydrothermal conversion of CR, WW, RW, ZB and LG were investigated at low to medium temperatures (75, 150, and 250 °C) and pressures (1, 50, and 240 bar), as seen in Figure 2, to establish the optimal conditions for hydrochar production at low temperatures.

Approximately 5.0 g of each biomass feedstock (CR, WW, RW, ZB, and LG) was placed between two layers of sieves (100 µm) into the steel reactor. Once pressure had been obtained, the flow rates were reduced to a minimal level (1-5 ml/min) The hydrothermal rig was then pressurised using a distilled water flow rate of 20 ml/min. The heat exchanger temperature was then set the target temperature (75, 150, and 250 °C). Once the system had stabilised at the desired conditions, the water flow rates were then introduced to the reactor with a flow rate of 20 ml/min. The total residence time of water in the reactor was determined about 1.9-2.3 min from pump to back pressure regulator. The liquid product stream was cooled to about 20-30 °C in a heat exchanger using a water stream and collected and then stored in a freezer at -18 °C for further analysis. The hydrochars were collected from the reactor and dried in an oven at 100 °C for overnight.

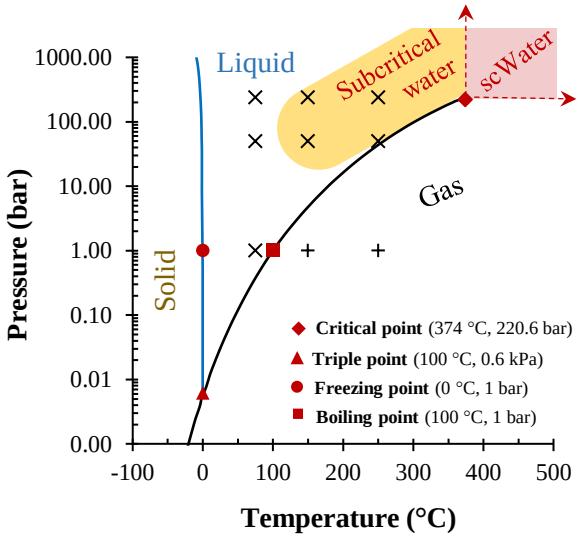


Figure 2. A schematic phase diagram showing Pressure – Temperature for water including the near and supercritical region (scWater). Plus (+) and Cross (x) signs represent the experiments investigated under vapour and liquid conditions, respectively.

2.2. Char formation and analysis

The yield of hydrochar (or solid residue) after each hydrothermal conversion experiments was determined using the following equation (Eq-1) [38].

$$Solid\ residue\,(wt.\%) = \frac{m_{char,dry}}{m_{biomass,dry}} * 100 \qquad (1)$$

Where, $m_{char,dry}$: the dried weight of hydrochar (g) after hydrothermal conversion, $m_{char,dry}$: the dried weight of biomass (g) before hydrothermal conversion.

2.3. Thermogravimetric Analysis

A thermogravimetric characterisation technique was used to measure the pyrolysis and then combustion behaviour of each biomass and hydrochar sample. This technique has been used to quantify components such as hemicellulose, cellulose [33]. A TA-Q500 system was loaded with approximately 15-25 mg of hydrochar (or raw biomass) using a platinum pan 4 mm deep and 10 mm in diameter. It was then heated from ambient temperature to 900 °C with a heating rate of 5.0 °C/min under N_2 flow rate of 100 ml/min and held at this temperature for about 5 minutes. N_2 was then replaced by air (to combust the fixed carbon) with a flow rate of 100 ml/min at 900 °C for a further 10 minutes [33]. The devolatilization behaviours of the biomass feedstocks and hydrochars were identified using the thermogravimetric (TG) and differential thermogravimetric (dW/dt) curves [39]. The fuel ratio was defined as the ratio of fixed carbon to volatile matter (dry ash free basis) for each biomass and hydrochar. Based on this technique, we propose a new method called "displacement" to characterize the impact of hydrothermal treatment. Displacement was determined with the global sum of all absolute value of the differences between the original and experimental DTG profiles as defined in Eq-2.

$$Displacement = \sum_{T=25°C}^{T=900°C} \left(\left| \left(\frac{dw}{dt} \right)_{bf,T} - \left(\frac{dw}{dt} \right)_{hc,T} \right| \right) \quad (2)$$

Where, T is the temperature of thermal decomposition (25-900 °C), $(dw/dt)_{bf,T}$ and $(dw/dt)_{ch,T}$ are the weight loss rate of biomass feedstocks and hydrochars at the specific temperatures in the thermal degradation process. Displacement is essentially a relative measurement and can be applied to any biomass and resultant char. A large displacement number means a large change in pyrolysis behaviour and this relates back to changes in organic composition [33, 40]. These displacement calculations are based on the dW/dt profiles shown in Figures 7,9,10,12 and 13. In essence, if the hydrochars profile is a close match to the original biomass then values of 1000-2000 tend to result. If the profiles show a marked difference in terms of in peak position (on the x-axis) or shape, then values of 5000-7000 tend to be seen.

3 Results and Discussions

3.1. Characterisation of feedstocks

Proximate analysis of the lignocellulosic biomass feedstocks (LG, ZB, WW, RW, and CR) is presented in Figure 3 and 4. Among these biomass feedstocks, the LG has the highest FC (~34 wt.%) and lowest volatile matter (~65 wt.%) ratios and ZB follow as second with the ~24 wt.% of fixed carbon and ~75 wt.% of volatile matter. WW and CR demonstrate relatively similar ratios ~15 wt.% of fixed carbon and ~83 wt.% of volatile matter with a low ash content (< ~2 wt.%). However, RW has a relatively high ash content (~15 wt.%) compared to the others. Furthermore, LG has the highest fuel ratio (0.52), while CR and WW both have the lowest fuel ratio at 0.19.

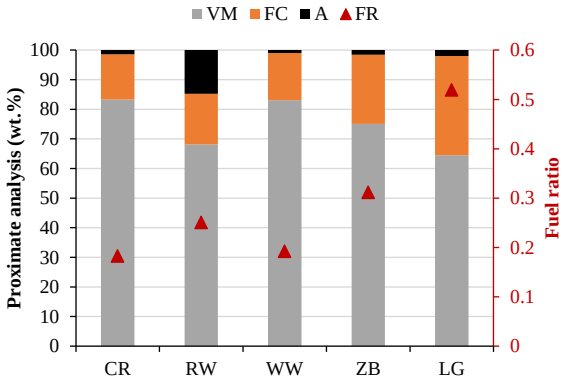


Figure 3. Proximate analysis (dry basis), fuel ratio (FR) of raw biomasses (CR-Coffee residue, RW-Rice waste, WW-White wood, ZB- Zilkha black, LG-Lignin).

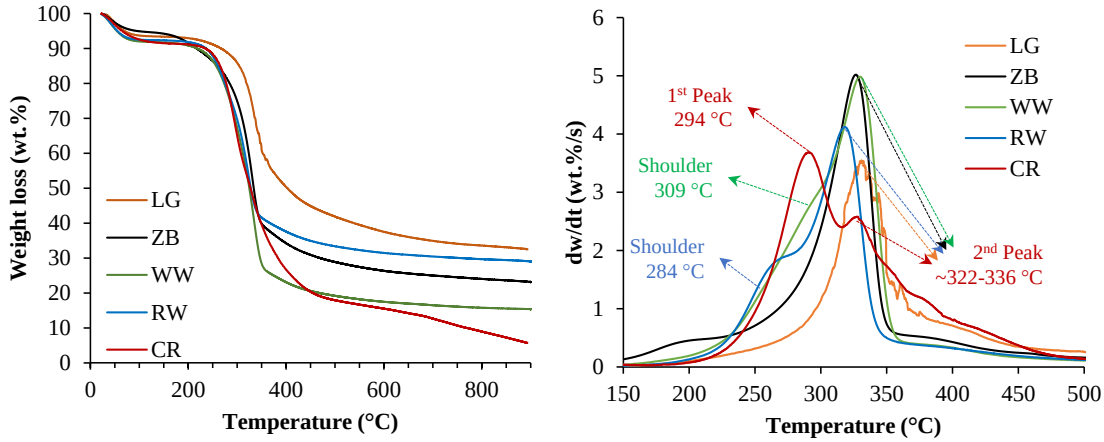


Figure 4. Weight loss and weight loss rates of the raw biomasses in slow pyrolysis (CR-Coffee residue, RW-Rice waste, WW-White wood, ZB- Zilkha black, LG-Lignin).

The lignocellulosic biomass consists of lignin (15-35 %, non-carbohydrate source), cellulose

and hemicellulose (carbohydrate sources), and potentially lipids and proteins [41]. Therefore, the thermal decomposition (slow pyrolysis) of the biomass feedstocks can provide detailed information about the biomass structures such as hemicellulose (220-315 °C), cellulose (315-400 °C), and lignin (160-900 °C) structures [33, 42, 43]. The DTG graph in Figure 4 demonstrates that LG and ZB provide only one strong peak at about ~330 °C, which demonstrates the high cellulose-lignin content. Furthermore, CR is the only biomass which demonstrates two clear peaks; the first one is at ~290 °C based on hemicellulose-cellulose structure and the second one is at ~330 °C based on the cellulose-lignin structures. Additionally, there is a strong tail after the second peak which indicates a high lignin content in CR. However, WW and RW provide one peak at ~322 °C (which is the structure of cellulose-lignin) with a detectable shoulder at 280-300 °C (originating from the hemicellulose-cellulose structures of WW and RW).

3.2. Solid residue-Hydrochar formation

After the hydrothermal conversion of biomass feedstocks (CR, WW, RW, ZB, and LG), the solid residue (or hydrochar) yields were determined using Eq-1. An increase in temperature decreases the solid residue yields at any pressure for all biomass types, as shown in Figure 5. Residual solids at temperatures up to 150 °C are quite high due to the low ratio of water-soluble components in the lignocellulosic materials. Pressure appears to have an insignificant impact on solubility at these temperatures. The water-soluble portion of the biomass disperses into the water at ~100 °C and hydrolysis starts at temperatures above 150 °C [44]. Each of the 5 biomass feedstocks consists of a different portion of water-soluble compounds at 75 °C. ZB has the highest water-soluble portion (~13-14 wt.%), while the other biomass feedstocks (CR, RW, WW and LG) have only ~2-7 wt.% of water-soluble portions. Conversely, the ratio of hydrolysed compounds at 150 °C is ~7-15 wt.% for CR while it is lower than 5 wt.% for the other biomass feedstocks. Biomass starts to carbonise at temperatures of 180-250 °C [17, 22, 25] as the cellulosic and hemicellulosic polymers disintegrates into monomers/oligomers [44].

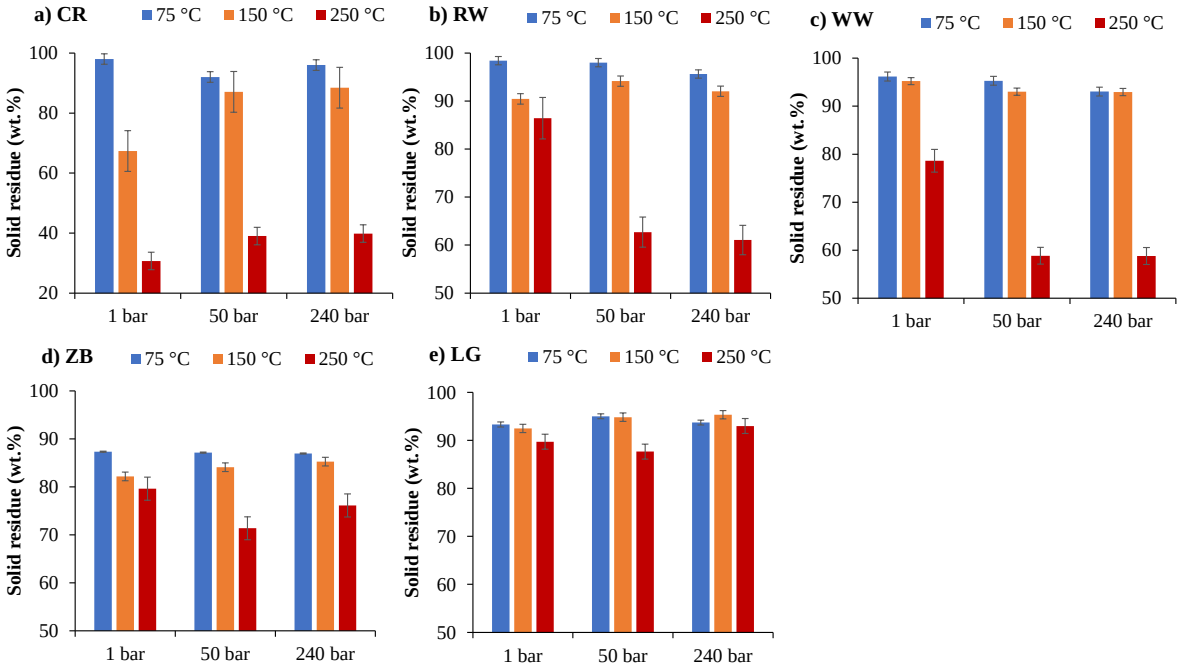


Figure 5. Solid residue (hydrochar) yields of biomasses; a) CR, b) RW, c) WW, and d) ZB and e) LG after the hydrothermal treatment at 75, 150, 250 °C and 1, 50, 240 bar.

CR has the lowest hydrochar yield (39 wt.%) at 250 °C and 50-240 bar and the dW/dt results (in Figure 4) show two clear peaks at ~290 °C and ~330 °C, which represent the higher hemicellulose-cellulose lower cellulose-lignin structures, respectively. The low hydrochar yield is due to the removal of the hemicellulose/cellulose fraction. LG, however, provides the highest hydrochar yield (87-92 wt.%) at relatively severe carbonisation conditions of 250 °C and 50-240 bar due to its low solubility and lack of hemicellulose and cellulose structures. ZB is also resilient to hydrothermal treatment with a high hydrochar yield (71-76 wt.%) at the same conditions. Figure 4 shows LG has a single thermal decomposition peak at ~336 °C. Similar to LG, ZB shows substantial low molecular weight materials evolving at low temperatures (150-225 °C). This could explain why more material solubilised into the water phase for ZB, even at relatively mild conditions. It is possible that the steam explosion breaks down the cell-wall to create lower molecular weight material which is more soluble. The strong peak at ~336 °C in LG and ZB arises from large amounts of cellulose-lignin structures.

Similarly, both RW and WW produce lower hydrochar yields (58-62 wt.%) than LG and ZB. Derivative plots for RW and WW show the presence of shoulder indicating the presence of hemicellulose-cellulose structures. The results provided in Figure 4 and 5 show that the lignocellulosic biomass feedstocks used in this study can be divided into three categories: (i)

high hemicellulose-cellulose, lower cellulose-lignin structures, (ii) low hemicellulose-cellulose, higher cellulose-lignin structures, (iii) cellulose-lignin only structures.

3.3. Thermal analysis of the hydrochars

3.3.1. High hemicellulose-cellulose, low cellulose-lignin structures (CR)

Figure 6 shows the proximate analysis of hydrochars (or solid residues) produced by the hydrothermal conversion of CR. The higher temperatures produce a higher ratio of VM and a lower ratio of FC compared to raw CR, which results in lower fuel ratios at higher temperatures (Figure 6). Furthermore, the ash content of hydrochars increased consistently particularly at high pressures.

Figure 7 presents the derivative weight loss rates of raw and hydrochars produced by the hydrothermal process of CR and the displacement at the process conditions. The degree of displacement relates directly to process temperature and pressure. Despite the noise in the weight loss rates at 250 ºC (in Figure 7a-c), there is a remarkable difference between the thermal decomposition profiles of the hydrochars produced at different conditions.

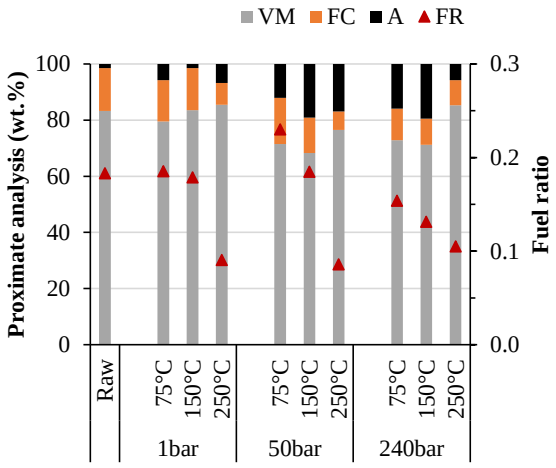


Figure 6. Proximate analysis (dry basis) of CR and hydrochars produced at the temperatures of 75-250 °C under the pressure of 1-240 bar. VM – Volatile Matter (db) FC – Fixed Carbon (db) A – Ash (db) FR – Fuel Ratio (dafb).

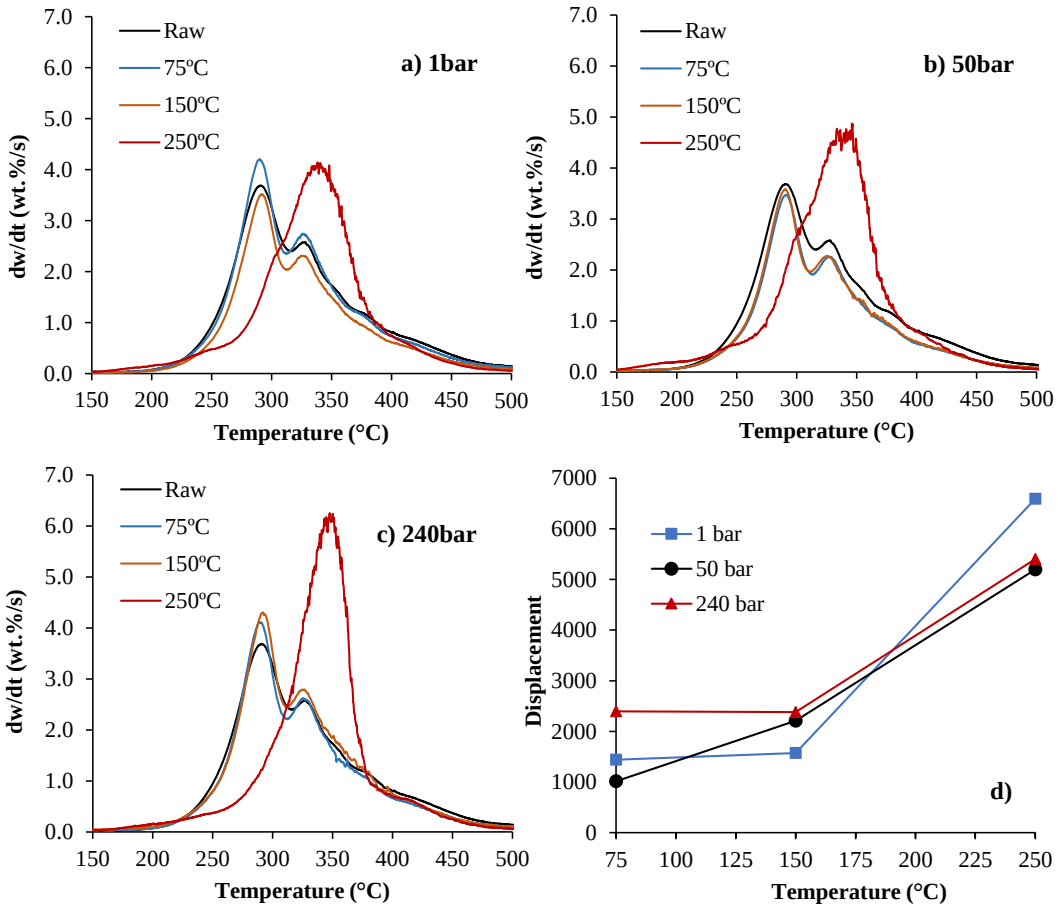


Figure 7. Weight-loss rates of raw and hydrochars (or solid residues) produced by the hydrothermal treatment of CR at a)1 bar, b) 50 bar, c) 240 bar and d) displacement at the hydrothermal process conditions.

The hydrochars produced at lower temperatures (75 °C and 150 °C) provides two characteristic weight loss rate peaks at ~290 °C and ~330 °C, which has the similar weight loss rates compare with the CR feedstock. Additionally, the displacements at these temperatures do not demonstrate a significant difference as shown in Figure 7d. However, hydrothermal conversion of CR at 250 °C produces a hydrochar with a single thermal decomposition peak at ~340-350 °C (Figure 7a-c) due to the cellulose-lignin only structures remaining after the hydrothermal treatment. Hemicellulose appears to have fully solubilized into the water at a temperature above ~160 °C, effectively under subcritical water conditions [25]. Since the hemicellulose is an amorphous heteropolysaccharide present as approximately 20-30 wt.% of the dry weight of most wood species. Hemicellulose forms hydrogen bonds with cellulose and covalent bonds with lignin (primarily α-benzyl ether bonds), and ester bonds with hydroxycinnamic acids and acetyl units [45]. The different

bonding in hemicellulose compared to cellulose, together with differences in crystallinity and molecular weight mean that the hemicellulose is more easily degraded under hydrothermal treatment, as seen in Figure 7a-c. The first peak disappeared due to a complete degradation of the hemicellulose structures from the CR at 250°C, 1-240 bar. The hydrochars produced at 250 °C, therefore, presents a mixture of low cellulose-high lignin structures, which could result in a higher heating value as lignin has a higher heating value than hemicellulose and cellulose [46]. The weight loss rate was 7.3, 4.5, and 6.0 wt.%/s at 250 °C and pressures of 1, 50, and 240 bar. Hydrochars produced at 250 °C, therefore, demonstrate a greater displacement ~5000-7000 as seen in Figure 7d.

3.3.2. Lower hemicellulose-cellulose, higher cellulose-lignin structures (RW and WW)

The proximate analysis of hydrochars (or solid residues) produced by the hydrothermal conversion of the biomasses having lower hemicellulose-cellulose and higher cellulose-lignin structures (RW and WW) are presented in Figure 8. Although there is a clear difference in ash content between RW and WW, these two lignocellulosic biomasses show similar levels of thermal decomposition, as a result of their similar hemicellulose, cellulose, and lignin compositions. RW and WW produce a hydrochar with a higher volatile matter and lower fixed carbon contents compared to untreated RW (Figure 8a) and WW (Figure 8b). RW has the highest ash content (~15 wt.%) compared with the other biomass feedstocks and the ash content does not change significantly after the hydrothermal treatment. RW ash is predominantly SiO_2 based and insoluble under hydrothermal conditions [47]. Pressure has no effect on the proximate composition of the hydrochars. At 250 °C there is an apparent increase in volatile content as a result of the removal of the hemicellulose component, (based on Figure 9a-c) which is not possible at lower temperatures without acid/alkali addition [48]. This increase is only relative to the overall composition of the biochar and caused by the insolubility of the SiO_2 in the RW and the increased solubility of the hemicellulose fraction at 250 °C.

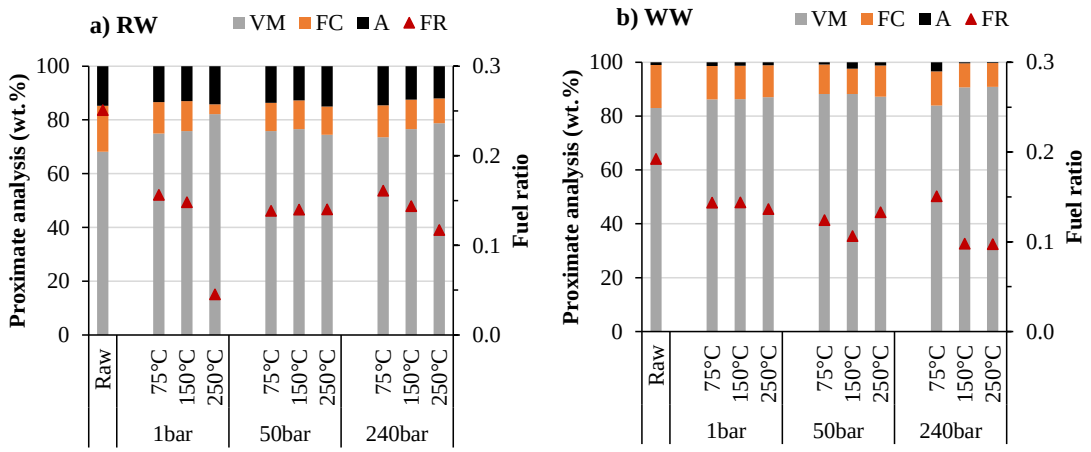


Figure 8. Proximate analysis (dry basis) of a) RW hydrochars and b) WW hydrochars produced at the temperatures of 75-250°C under the pressure of 1-240 bar. VM – Volatile Matter (db) FC – Fixed Carbon (db) A – Ash (db) FR – Fuel Ratio (dafb).

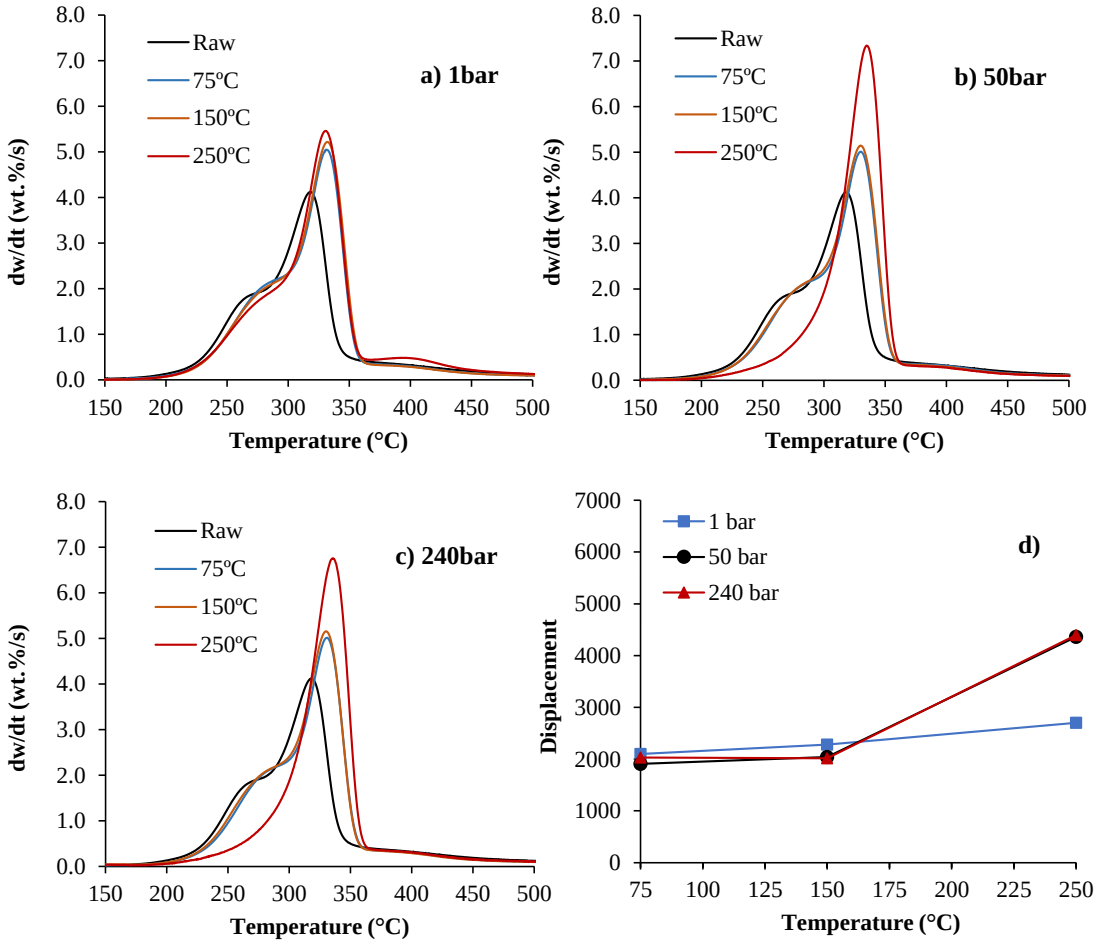


Figure 9. Weight-loss rates of raw and hydrochars (or solid residues) produced by the hydrothermal process of RW at a) 1 bar, b) 50 bar, c) 240 bar and d) displacement at the hydrothermal process conditions.

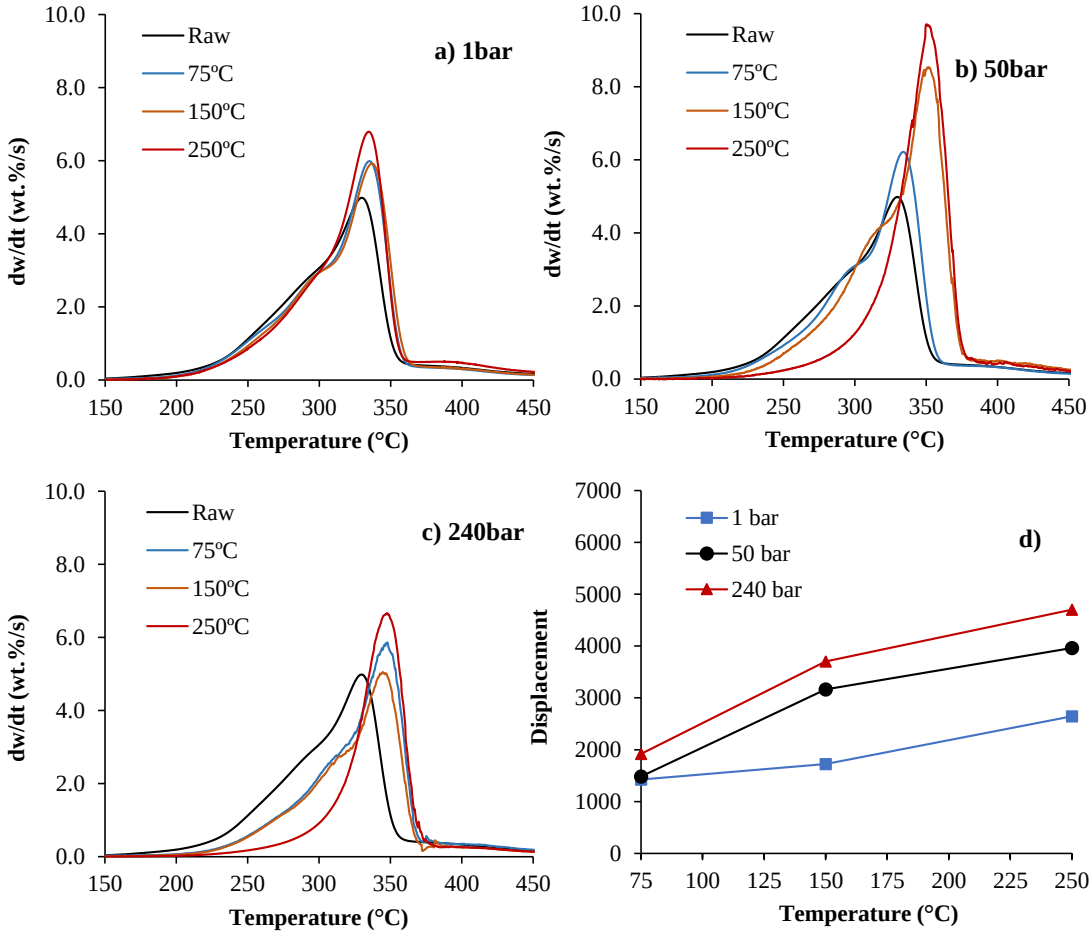


Figure 10. Weight-loss rates of raw and hydrochars (or solid residues) produced by the hydrothermal process of WW at a) 1 bar, b) 50 bar, c) 240 bar and d) displacement at the hydrothermal process conditions.

The weight-loss rates and the displacements of RW and WW hydrochars are presented in Figure 9 and Figure 10, respectively. The thermal decomposition of RW hydrochars show a small detectable shift from 322 °C to 333-340 °C as seen in Figure 9a-c. The hydrochars produced at lower temperatures (75 °C and 150 °C) provides similar trends with the raw RW, a strong peak at ~333 °C with a weight loss rate of ~5.2 wt.%/s, (cellulose-lignin) and a shoulder at lower temperatures of ~304 °C (hemicellulose-cellulose) of 2.3 wt.%/s (Figure 9a-c). The hemicellulose-cellulose levels in RW and WW are much lower than in CR. Therefore, it appears as a peak in the decomposition of CR (Figure 7a-c) while it is only a shoulder in the decomposition of RW (Figure 9a-c) and WW (Figure 10a-c). The hemicellulose and cellulose structures were degraded and solubilised above ~160 °C and ~220 ºC, respectively, under subcritical water conditions [25, 44] due to the catalytic effect of hydroxyl (OH-) and hydronium (H+) ions. The shoulder (hemicellulose-cellulose) disappeared at 250 °C and 50-

240 bar. The displacement (Figure 9d) also demonstrates the similarity with the thermal decomposition of the solid residues at low temperatures (75 °C and 150 °C) and changes seen at higher temperatures (250 °C). Neither pressure nor temperature has a significant effect on the solid residues produced at lower temperatures (75 °C and 150 °C), while a significant difference was observed for the hydrochars produced at higher temperatures of 250 °C. The WW hydrochar derivative plots also show a shift to the higher temperature from 333 °C to 340 °C at 1 bar (Figure 10a) and a further shift to ~350 °C at 50 bar and 240 bar (Figure 10b and 10c). The weight-loss rates are ~6.0 wt.%/s at low hydrothermal temperatures (75 °C and 150 °C) and increased to ~6.8 wt.%/s with the temperature increase to 250 °C at 1 bar. The hydrochars produced at 75 °C and 150 °C indicate the shoulders which indicate the presence of hemicellulose-cellulose structures. However, the shoulder disappeared at 250 °C, at 50 bar and 240 bar (Figure 10a-c), which is characteristically similar to RW.

3.3.3. High cellulose-lignin structures (ZB and LG)

Figure 11 shows the proximate analysis of the hydrochars produced by the ZB and LG, which have a high level of cellulose-lignin structures. These biomasses (ZB and LG) are defined as having higher FC and lower VM compare to other biomasses, which results in higher fuel ratio and potentially higher heating value due to higher levels of lignin. The proximate composition of these two biomass types show insignificant changes during hydrothermal treatment at 75-250 °C. The small differences could be therefore attributed to the absence of hemicellulose structures which usually decompose at ~180-200 °C.

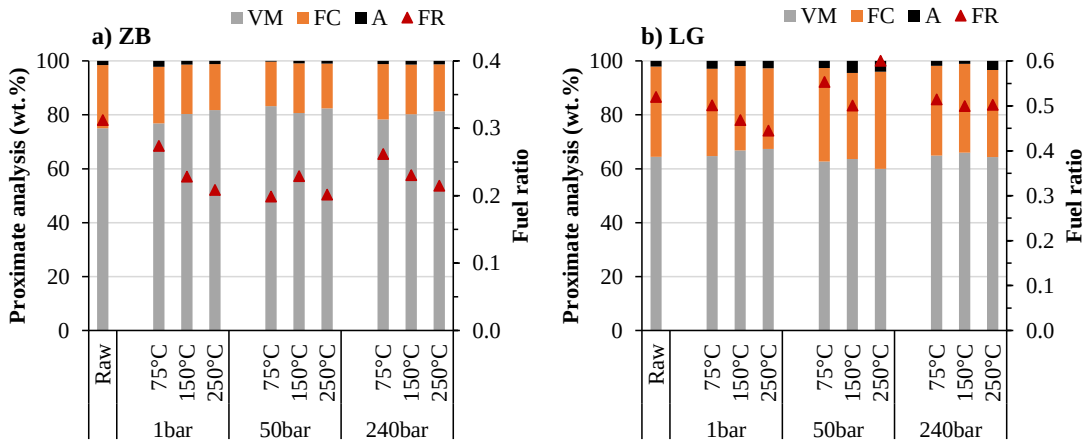


Figure 11. Proximate analysis (dry basis) of a) ZB hydrochars and b) LG hydrochars produced at the temperatures of 75-250°C under the pressure of 1-240 bar. VM – Volatile Matter (db) FC – Fixed Carbon (db) A – Ash (db) FR – Fuel Ratio (dafb).

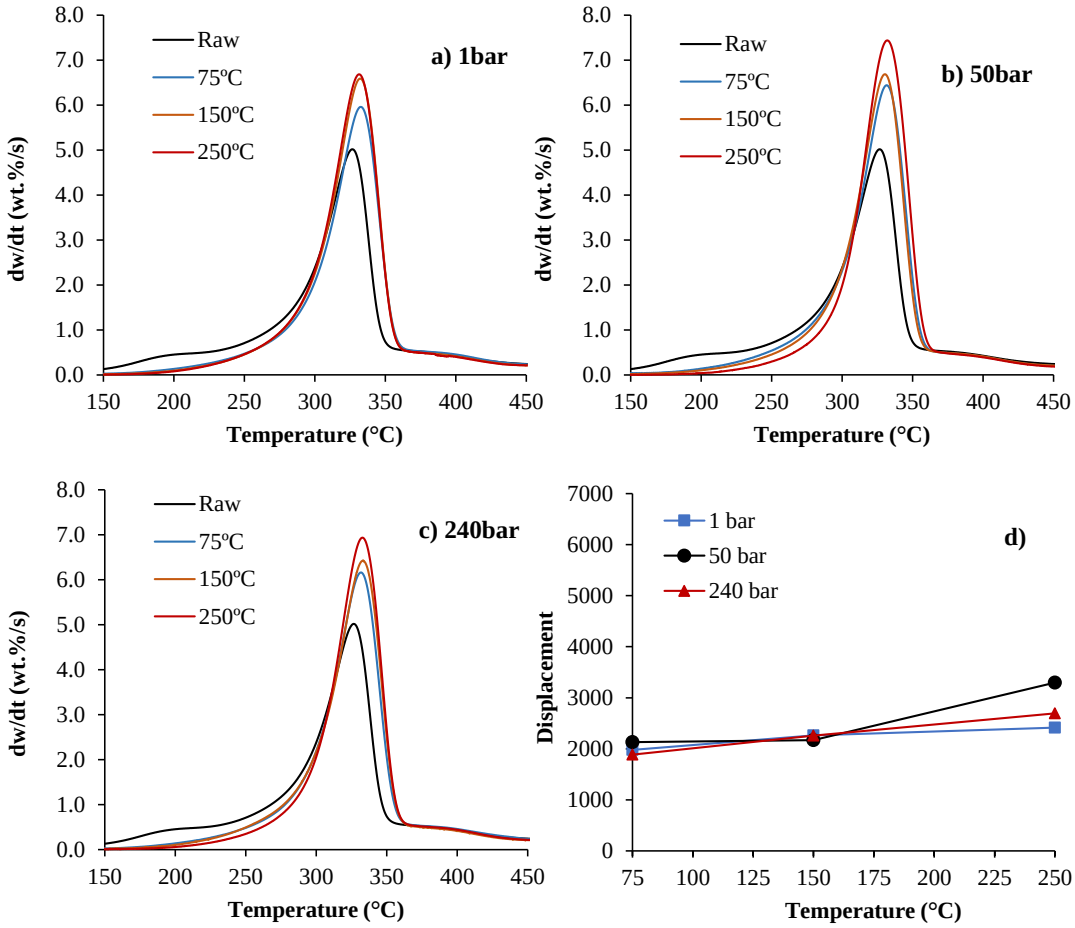


Figure 12. Weight-loss rates of raw and hydrochars (or solid residues) produced by the hydrothermal process of ZB at a) 1 bar, b) 50 bar, c) 240 bar and d) displacement at the hydrothermal process conditions.

The thermal decomposition of the ZB and LG provides only one peak at ~330 °C, indicating that minimal hemicellulose is present. The thermal decomposition of the hydrochars produced by ZB shows a slight shift to a higher temperature of ~336 °C (Figure 12); however, the hydrochars produced by LG provide similar thermal decomposition profiles compare with the LG (Figure 13). The slight shift in the ZB hydrochars could be attributed to the decomposition of cellulose. However, LG hydrochars have cellulosic material and therefore did not provide any shift in the thermal decomposition, proving that neither pressure nor temperature had a significant effect on hydrochars generated from biomass with a high lignin content (Figure 13). The weight-loss rates of ZB hydrochars are ~6-8 wt.%/s when treated at >75 ^{o}C and do not show any significant change as pressure changes, as shown in Figure 12. However, the LG hydrochars show little difference in weight loss rates at any temperature or pressure, as shown in Figure 13. Unlike CR, WW, RW, ZB and LG both produce minimal displacements (Figure

12d and 13d) during hydrothermal conversion, which can be attributed to the high levels of lignin in ZB and LG. Lignin is an amorphous natural polymer made up of aromatic blocks which are cross-linked by carbon and ether linkages and considered to be hydrophobic due to its low solubility in water.

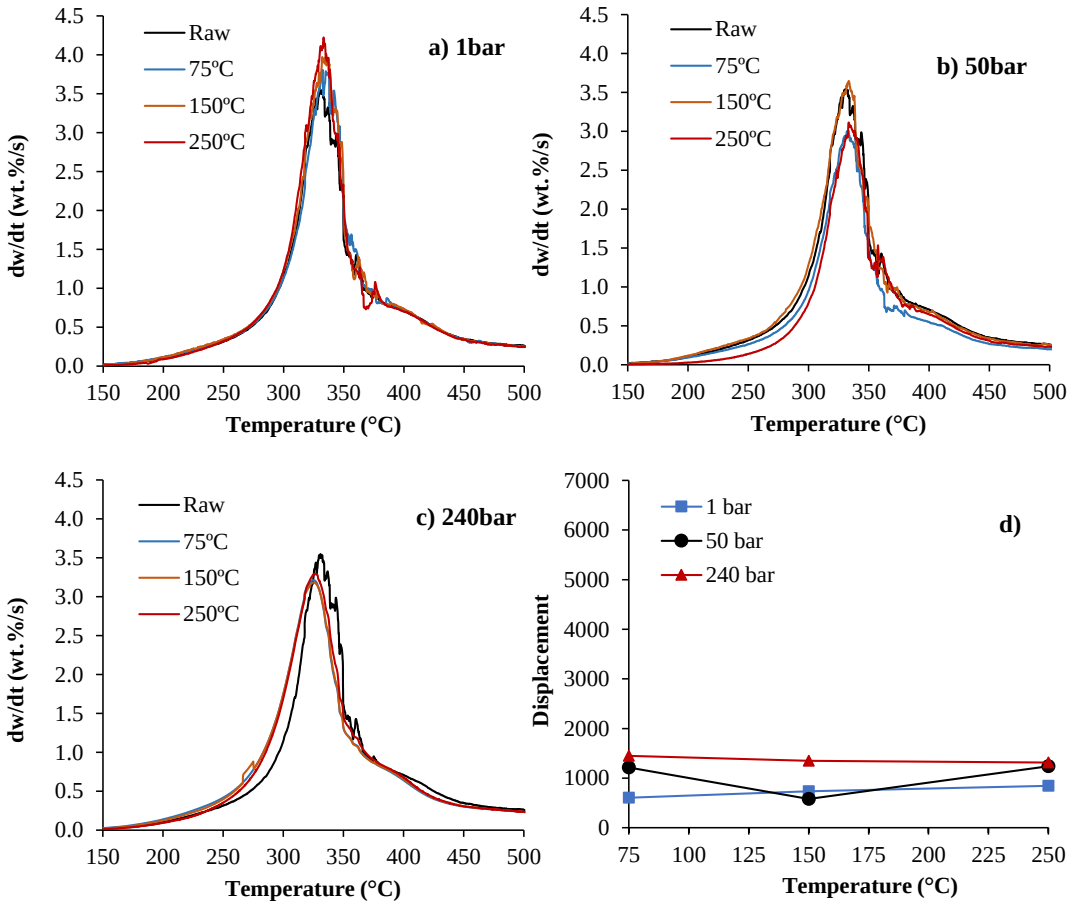
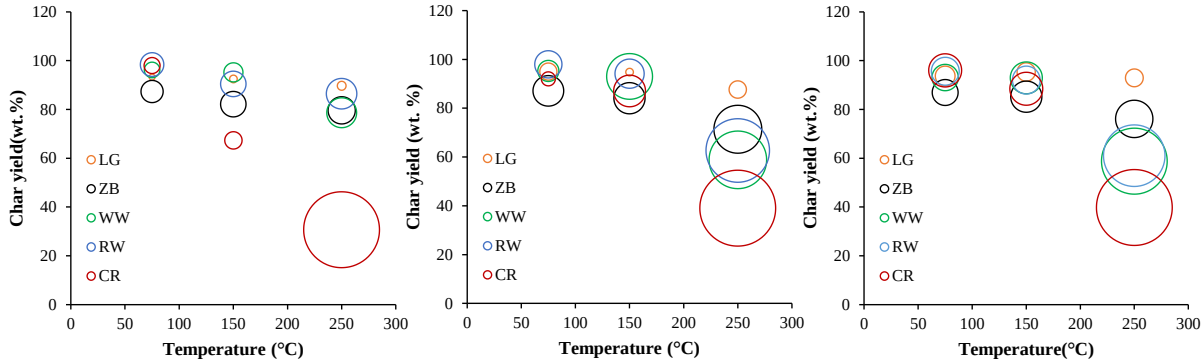


Figure 13. Weight-loss rates of raw and hydrochars (or solid residues) produced by the hydrothermal process of LG at a) 1 bar, b) 50 bar, c) 240 bar and d) displacement at the hydrothermal process conditions.

3.4. Relationship between Char yield and Displacement

Figure 14 shows the relationship between char yield and displacement at the specific temperature and pressure conditions of hydrothermal treatment. The differences in the relationship between char yield and displacement of the biomass categories were clearly demonstrated in Figure 14. Hydrochars produced at lower temperatures (<150 °C) show relatively small displacements while the hydrochars produced at higher temperature (200 °C) showed relatively higher displacement.



a) P = 1 bar **b) P = 50 bar** **c) P = 240 bar**

Figure 14. Relationship between char yield and displacement values under the hydrothermal treatment conditions. The width of bubbles represents the displacement value at each temperature (x axis, 75, 150, 250 °C) and pressure (a) 1 bar, b) 50 bar, c) 240 bar)

The highest decomposition and displacement were observed for category (i) biomass feedstocks (CR (red bubbles)) at 250 °C at all pressures. Category (ii) biomass feedstocks (RW (blue bubbles) and WW (green bubbles)) demonstrated the second highest decomposition and displacement, as both hemicellulose and cellulose structures in category (i) and (ii) were successfully degraded under subcritical conditions. The robust lignin structures in category (iii) biomass feedstocks (ZB (black bubbles) and LG (orange bubbles)) resulted in the lowest decomposition and displacement at any temperature and pressure of hydrothermal treatment compared to other two categories. The increase in pressure slightly increases the displacement level of the biomasses at a low temperature (75 °C and 150 °C).

4. Conclusions

This study explored the hydrothermal treatment of biomass in a semi-continuous flow rig. The solid residues at <150 °C and <240 bar did not show any significant structural changes compared with the untreated biomass feedstocks. However, the hydrochars produced at 250 °C and 50 240 bar demonstrates significant structural modifications depending on the biomass type. The first category provided relatively low hydrochar yield (~39 wt.%) due to the degradation of higher hemicellulose-cellulose structures. The second category demonstrated relatively higher hydrochar yields (58-62 wt.%) compared to (i). Category (iii) had the highest hydrochar yields (~73 wt.% for ZB and ~90 wt.% for LG) due to the absence of hemicellulose and generally lower cellulose. The novel displacement analysis method produced a similar trend. Biomass with a higher hemicellulose content produced the highest levels of displacement, with the least displacements resulting from the highest lignin samples. The “displacement”

method could thus be a new characterisation technique for the hydrochars to show the quantitative impact of hydrothermal treatment.

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