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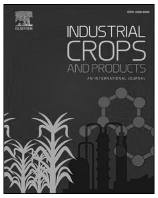

Molten salt biomass torrefaction – A sensitivity analysis of process conditions

Lee Kohlin [a], Hayden Pritchard [b], Adam C. Gladen [a], Behrooz Dehkordi [a], Dilpreet Bajwa [b,*]

[a] *Department of Mechanical Engineering, North Dakota State University, Fargo, ND, USA*
[b] *Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, MT, USA*

A R T I C L E I N F O

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A B S T R A C T

Biomass is an abundant renewable resource that can be upgraded via torrefaction. Molten salts catalyze the torrefaction reaction, creating enhanced products for fuel and soil amendment purposes at lower temperatures than inert gas torrefaction. The objective of this study is to elucidate the main effects of molten salt torrefaction process conditions on ponderosa pine (*Pinus ponderosa*) and cave in rock switchgrass (*Panicum virgatum*) in a binary salt blend of lithium nitrate and potassium nitrate using a Plackett-Burman screening analysis. The investigated process conditions include sweep gas, temperature, salt to biomass ratio (S-B ratio), residence time, and lithium content. The metrics used to evaluate torrefaction severity include mass yields, chemical composition (lignin, cellulose, hemicellulose, extractives), higher heating value (HHV), carbon and nitrogen content, pH, and water sorption. The results show that switchgrass is more severely torrefied through molten salt torrefaction than pine at the same process conditions. For example, switchgrass mass yields are on average 23.3 % lower than pine mass yields across the test conditions. For both feedstocks, the most impactful process conditions are temperature, time, and lithium content in that order with some exceptions. For instance, the effect of temperature, time and lithium content on HHV are, respectively, 3.4×, 2.3×, and 1.7× larger than the next largest process condition for pine, whereas for switchgrass, these values are 3.6×, 2.7×, and 1×. Particle size, sweep gas, and S-B ratio have minor effects depending on the metric, but are overall not significant compared to temperature. The data suggests that an inert gaseous environment need not be maintained to facilitate molten salt torrefaction. Additionally, molten salt torrefaction can produce torrefied biomass with slightly different characteristics than inert gas torrefaction.

1. Introduction

Focus on renewable resources is intensifying as global energy demands rise along with CO_2 emissions (Jackson et al., 2019). As such, much research has been conducted on developing technologies for replacing fossil-fuel-based energy sources and for developing sustainable products from renewable biomass resources. Biomass is accessible to most communities and it accounts for the largest renewable energy source in the world (Niu et al., 2019; IEA., 2023). It can be combusted as an alternative to fossil fuels for heat and power, or used as a feedstock to produce higher quality liquid and gaseous biofuels. Furthermore, biomass can be converted to biochar and used as a soil amendment. Biochar can improve plant and soil health by promoting plant growth, water retention, and microbial activity (Hunt et al., 2010). Additionally, when used for soil amendment, biochar sequesters CO_2 by storing recently absorbed CO_2 into soils as stable carbon (Singh et al., 2010; Edmunds, 2012).

Although biomass is an attractive renewable resource, there are inherent drawbacks which limit its potential, namely its hydrophilicity, fibrous composition, high moisture content, low energy density, and poor grindability (Niu et al., 2019; Repellin et al., 2010; Singh et al., 2010; Tumuluru et al., 2021; Edmunds, 2012). One remedy to these drawbacks is torrefaction, a mild thermochemical treatment traditionally done in a low-to-zero oxygen environment at temperatures from 200 to 300 °C (more commonly between 240 and 280 °C), for 10 minutes to 3 h (Niu et al., 2019; Shankar Tumuluru et al., 2011; Tumuluru et al., 2021). Typically, the energy required for this process is provided by combusting a portion of the biomass feedstock, or by using an outside fuel source which consequently reduces the sustainability of the process and produces additional carbon emissions (Bergman et al., 2005).

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* Corresponding author.
E-mail address: Dilpreet.bajwa@montana.edu (D. Bajwa).

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To upgrade the thermal processing of biomass, studies have investigated using molten salts to facilitate processing at lower temperatures and to improve the end products. Enhanced reactivity and improved heat transfer by use of alkali carbonates have been reported for steam gasification of lignocellulosic biomass (Hathaway et al., 2013). Additionally, molten alkali salts have been shown to reduce pyrolysis temperatures by acting as an improved heat transfer medium and catalyst to the biomass decomposition reaction (He et al., 2022; Yang et al., 2022, 2020). Yang et al. investigated low temperature pyrolysis at 300 °C with a ternary salt blend ($NaNO_3$-KNO_3-$NaNO_2$) and found a catalytic effect due to the salts which was attributed to both the alkali metal cations and the anions (Yang et al., 2020). The majority of molten salt biomass treatment studies cover higher temperature treatments such as pyrolysis and gasification, focusing on the liquid and gaseous products (Nygård and Olsen, 2012). There is limited information about the solid products produced. Recently, torrefaction in molten salts below 300 °C has been investigated (Backer and Gladen, 2023; Wang et al., 2021). These studies show that using molten salts provides a higher degree of torrefaction compared to inert gas torrefaction. Wang et al. found molten salt torrefaction of oleifera shell to be a superior pretreatment for pyrolysis than hydrothermal and inert gas torrefaction at the same temperature and residence time. The resulting energy density, fixed carbon, and lignin contents of the salt torrefied oleifera shell were shown to be much greater than those of inert gas torrefied oleifera shell under the same conditions (Wang et al., 2021). Similar results were reported by Backer, and Gladen, who also showed molten salt torrefaction to be more sensitive to temperature than inert gas torrefaction for ponderosa pine over the range of temperatures considered (Backer and Gladen, 2023). Additionally, Backer and Gladen, found that lithium cations are the most catalytic of the alkali metals, followed by sodium, then potassium. As such, the decreasing catalytic activity corresponds to increasing atomic radius of the cation.

As a nascent field, there is a knowledge gap on how the process conditions involved with molten salt torrefaction impact the torrefied product and on how herbaceous biomass responds to the treatment. Prior molten salt torrefaction studies have focused on the effect of temperature and salt composition on a single, non-herbaceous feedstock. However, from studies on inert gas torrefaction, it is known that, beside temperature, key process variables include residence time, sweep gas composition (inert versus oxidizing), and particle size. For inert gas torrefaction, temperature and residence time are the most dominant process conditions (Nhuchhen and Basu, 2014; Phusunti et al., 2018; Strandberg et al., 2015). Temperature is a key variable because the lignocellulosic polymers decompose in specific temperature ranges. In inert gas torrefaction, hemicellulose decomposes at 200–250 °C, cellulose at 240–350 °C, and lignin at 280–500 °C (Niu et al., 2019; Shankar Tumuluru et al., 2011; Trubetskaya et al., 2020). Prins et al. (2006) reports that increasing the residence time allows for a more thorough decomposition, however, doubling the residence time is less effective than increasing temperature by 20 °C. When considering sweep gas, inert gas such as nitrogen is used to prevent the redox combustion reaction. For torrefaction in a gaseous environment, the effects of sweep gas (air or nitrogen) are shown to become more significant as temperature increases (Nhuchhen and Basu, 2014). Huang et al. (2021) discovered sweep gas to be more sensitive on herbaceous feedstocks with recorded mass yields of 93.26 %, 84.53 %, and 37.60 % for herb residues torrefied in nitrogen, air, and oxygen respectively, at 200 °C for 30 minutes. Particle size can affect the heat transfer rates and reaction kinetics during torrefaction (Peng et al., 2012). Smaller particles are more susceptible to the effects of torrefaction due to lower conduction resistance, ease of internal vapor diffusion, and increased cellulose exposure. Although, for inert gas torrefaction, particle sizes below 1 mm do not have a significant impact on torrefaction severity, especially compared to temperature and time (Peng et al., 2012; Trubetskaya et al., 2020). For molten salt torrefaction, the relative impact of these process variables, and of new variables introduced by the presence of molten salts, e.g. lithium content, on torrefaction severity has not yet been investigated. Nor has been feedstock type.

As such, the present study aims to explore the effects of molten salt torrefaction processing conditions on cave in rock switchgrass and ponderosa pine in a molten binary salt blend of lithium nitrate and potassium nitrate. The selected process conditions are torrefaction temperature, residence time, lithium content, particle size, sweep gas, and salt-to-biomass ratio. Using a Plackett-Burman screening analysis, the effects of the process conditions on the characteristics of the solid torrefied biomass products are determined. The research will help address the process condition knowledge gap by investigating the relative importance of torrefaction variables for two different feedstocks, one herbaceous and one non-herbaceous.

2. Materials and methods

2.1. Materials

Ponderosa pine (*Pinus ponderosa*) was purchased from Valley Hardwood Supply (Dilworth, MN, USA). Cave in rock switchgrass (*Panicum virgatum*) was obtained from University of Missouri (Columbia, MO, USA). The raw feedstock was reduced by a multi-purpose high speed grinder and sieved to particle sizes of 250–500 μm, and 710–850 μm (Fig. 1). The pine and switchgrass were dried at 120 °C for 2 h prior to torrefaction. All dried feedstock was stored in a dry nitrogen environment to prevent humidity absorption. Lithium nitrate (reagent grade) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium nitrate (99 % purity) was purchased from Thermo Fisher Scientific (Waltham, MA, USA). Both salts were received in anhydrous crystalline powder form. The composition of the two salt blends were (35 % $LiNO_3$ - 65 % KNO_3) and (45 % $LiNO_3$ - 55 % KNO_3) by weight percent (%wt). Each salt component was measured using an analytical scale, then blended to homogenize. The salt mixture was melted at a temperature of 350 °C until complete transition to a liquid phase. After melting, the salts were cooled to room temperature and ground into a powder.

2.2. Screening design

A 16-run Plackett-Burman Screening Analysis (PBSA) matrix was used to evaluate the sensitivities of the process conditions on torrefaction severity for molten salt torrefaction. The PBSA matrix and analysis method used in the current study were adopted from the methods outlined by (Beres and Hawkins, 2001). Table 1 provides the process conditions and their respective high and low levels. The high and low levels represent the conditions that are hypothesized, based on inert gas torrefaction and prior molten salt torrefaction data, to result in more or less severely torrefied biomass, respectively. Thus, the high levels include higher temperature (Phusunti et al., 2018), longer residence time (Prins et al., 2006), smaller particle size (Peng et al., 2012), higher lithium content (Backer and Gladen, 2023), inert sweep gas (Nhuchhen and Basu, 2014), and higher salt-to-biomass ratio (Backer, 2018). The PBSA matrix, showing the pattern of the higher and lower process condition levels, is provided in Table 2. The matrix is populated by the values corresponding to the high and low levels for the process conditions, developing 16 unique test conditions. The effect of a process condition for a given metric is calculated using Eq. (1),

$$Effect_j = \frac{\sum_{i=1}^{16} y_i m_{j,i}}{d} \tag{1}$$

where i and j are the test number and process variable, respectively, y_i is the value of the torrefied biomass metric (e.g. mass yield, higher heating value), $m_{j,i}$ is the PBSA matrix value (+1 or −1) corresponding to + or – from Table 2, and d is the design size of 8. The effect, $Effect_j$, represents the average (over all test conditions) change in the metric for the given

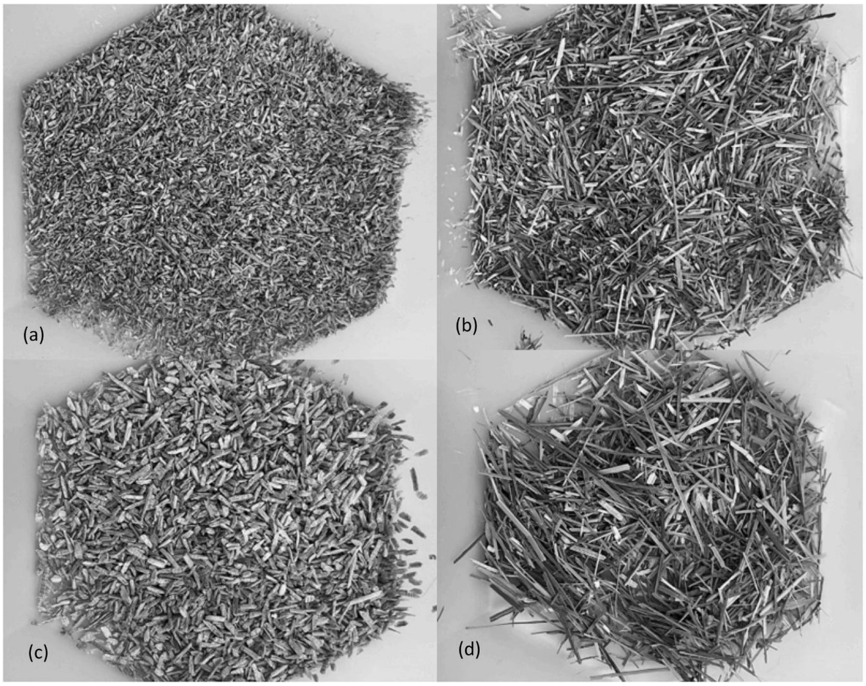


Fig. 1. Photographs of the raw biomass feedstocks. (a) 250–500 μm pine, (b) 250–500 μm switchgrass, (c) 710–850 μm pine, (d) 710–850 μm switchgrass.

Table 1
Process conditions higher and lower levels.

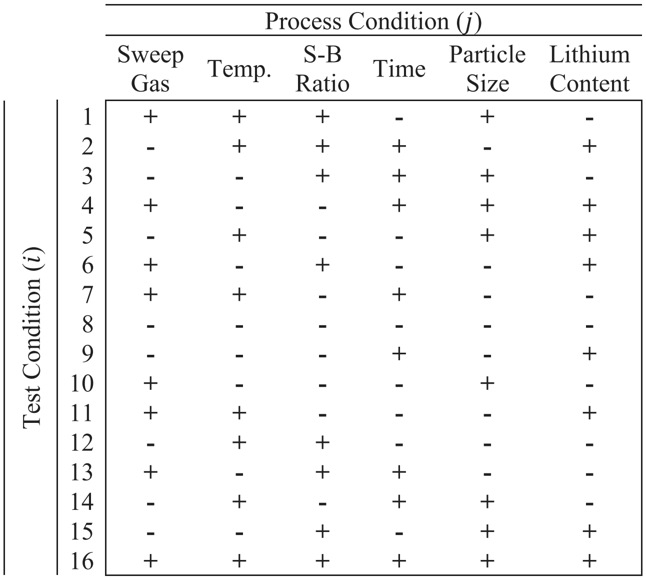
Process condition	Higher (+)	Lower (-)
Sweep Gas	Nitrogen	Air
Temperature	225 °C	200 °C
Salt-to-Biomass Ratio	20:1	15:1
Time	2 h	30 minutes
Particle Size	250 – 500 μm	710 – 850 μm
Lithium Content	45 % (55 % KNO_3)	35 % (65 % KNO_3)

change in the process condition level, e.g. the effect for the higher heating value with regards to temperature equals the average change in higher heating value for a 25 °C change in torrefaction temperature (225 °C vs 200 °C). For metrics that are percentage values (e.g. mass yield%) the effect represents a change in percentage points (%-points) per change in process condition.

2.3. Torrefaction methodology

The torrefaction and washing methodology was adapted from the methods developed by (Backer and Gladen, 2023; Backer, 2018). All samples were torrefied in an STF-1200 tube furnace (Across International, Livingston, NJ, USA). Three grams of the feedstock were placed

Table 2
Plackett–Burman screening analysis (PBSA) matrix.



		Process Condition (*j*)					
		Sweep Gas	Temp.	S-B Ratio	Time	Particle Size	Lithium Content
Test Condition (*i*)	1	+	+	+	-	+	-
	2	-	+	+	+	-	+
	3	-	-	+	+	+	-
	4	+	-	-	+	+	+
	5	-	+	-	-	+	+
	6	+	-	+	-	-	+
	7	+	+	-	+	-	-
	8	-	-	-	-	-	-
	9	-	-	-	+	-	+
	10	+	-	-	-	+	-
	11	+	+	-	-	-	+
	12	-	+	+	-	-	-
	13	+	-	+	+	-	-
	14	-	+	-	+	+	-
	15	-	-	+	-	+	+
	16	+	+	+	+	+	+

into a (45 × 20 × 100 mm) alumina crucible boat with its designated S-B ratio (20:1 or 15:1) and salt blend (35 % $LiNO_3$ or 45 % $LiNO_3$), following the PBSA design. The feedstock and powdered salt were dry mixed prior to placement in the crucible. Before torrefaction began, the desired sweep gas was allowed to fill the tube to ensure the torrefaction took place in the prescribed environment. Ultra-high purity nitrogen or filtered, dry air continuously swept the reactor at 100sccm. The appropriate heating program was selected for torrefaction following the PBSA matrix. The heating program was consistent for all samples, only changing the end condition based on the residence time and torrefaction temperature. The heating program involved heating the sample to 161 °C, followed by a 10-minute isotherm at 161 °C, which is above the melting point of both salt blends (Carveth, 1898). The samples were then heated to the designated torrefaction temperature (200 °C or 225 °C) at 1 °C/min followed by an isotherm for the designated residence time (30 min or 2 hr). The samples were cooled to room temperature before removal from the tube furnace. After torrefaction, the solid biomass-salt block was thoroughly washed in distilled water to separate the biomass from the salt. The wet, torrefied biomass was dried at 120 °C for 2 h to become bone dry. For comparison, samples were torrefied in nitrogen at 200, 220, 240, 260, 280, 300, and 320 °C for 2 h.

2.4. Torrefaction severity metrics

The severity of torrefaction was characterized by assessing the metrics of mass yield, chemical composition, higher heating value (HHV), carbon and nitrogen content, pH, and water sorption of the torrefied biomass. Mass yields were calculated by Eq. (2).

$$MY\% = \frac{mass\ of\ solid\ product}{mass\ of\ raw\ dry\ sample} \times 100 \tag{2}$$

Lignocellulosic composition (lignin, cellulose, hemicellulose) were analyzed according to the National Renewable Energy Laboratory (NREL) Laboratory Analytical Procedure (LAP): Determination of Structural Carbohydrates and Lignin in Biomass (Sluiter et al., 2008). Acid-soluble concentrations were measured on a Bio-rad Aminex 87-H column (Hercules, CA, USA). The carbohydrates within lignocellulosic biomass encompass cellulose and hemicellulose, which when addressed together, will be referred to as holocellulose hereafter. Higher heating value was measured by oxygen-bomb calorimetry, using a Parr 6200 Isoperibol Calorimeter (Parr Instruments, Moline, IL, USA), following the manufacturer's guidelines. Reference benzoic acid tablets were measured throughout HHV measurements to ensure accuracy and precision. Carbon and nitrogen content were determined by combusting samples in a Costech ECS 4010 gas chromatograph (Valencia, CA, USA). The pH values were obtained by measuring a biomass-water solution using a Mettler Toledo Seven Easy pH Meter (Columbus, OH, USA). Samples were soaked in DI water until <50 % of the biomass remained floating, or a maximum of 5 days. Water uptake was measured by soaking 0.1 g of oven-dry sample in DI water for an hour followed by a straining process using a Speedball 110 Mono 47 μm mesh screen. Excess water was shaved off the bottom of the mesh before weighing. Water uptake was calculated as a mass ratio of water absorbed over initial dry weight using Eq. (3).

$$Water\ uptake = \frac{Mass\ of\ wet\ sample - Mass\ of\ dry\ sample}{Mass\ of\ dry\ sample} \tag{3}$$

Due to the limited quantity of molten salt torrefied material, the reported uncertainty for the molten salt torrefied samples is calculated using the instrument uncertainty reported at 95 % confidence interval. However, to estimate the uncertainty associated with the feedstock, larger batches of inert gas torrefied feedstocks were torrefied at 240 and 280 °C for pine and 260 and 300 °C for switchgrass, because these temperatures have similar mass yields as the molten salt torrefied feedstocks. The metrics of chemical composition, HHV, pH, and water uptake were measured at least three times for these inert gas torrefied samples. This data was then used to calculate the uncertainty at 95 % confidence interval for the metrics for those samples.

3. Results and discussion

3.1. Mass yields

Fig. 2 shows the mass yields of molten salt torrefied samples and inert gas torrefied controls, as well as the main effects of the process conditions on mass yield. As shown in Fig. 2a, all samples have reductions in mass yields as volatile compounds and moisture evolved during the torrefaction process. However, from the molten salt treatment, switchgrass has consistently and substantially lower mass yields than pine. For example, the least severely torrefied pine sample has a mass yield of 91 % while the least severely torrefied switchgrass has a mass yield of 68 %. Additionally, the average mass yield for the torrefied switchgrass is 58.7 % while the average mass yield for the torrefied pine is 76.5 %. The large gap in mass yields between the two feedstocks suggest that the molten salt treatment has a more prominent impact on devolatilizing switchgrass than pine. This hypothesis is supported by the fact that, at the same temperature, mass yields between the two feedstocks are similar for inert gas torrefaction as shown in Fig. 2c. Although

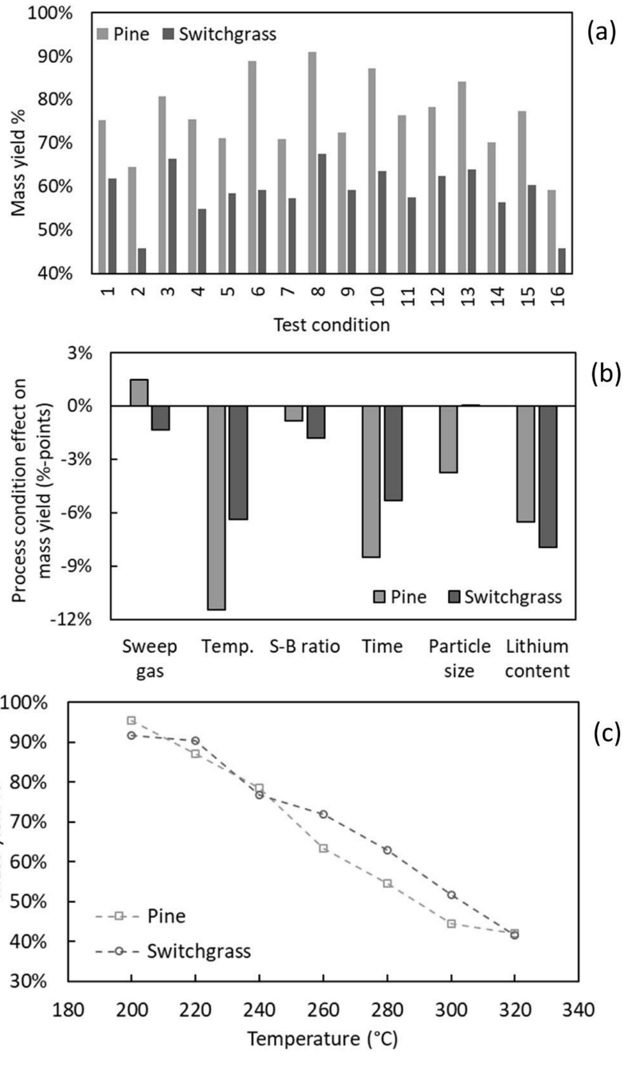


Fig. 2. Mass yield and process condition effects on biomass torrefaction. (a) Experimental pine and switchgrass (b) Effects of process conditions on mass yield (c) Control pine and switchgrass.

switchgrass is more amenable to the molten salt treatment, pine has a wider range of response to the process conditions. This wider range of response is illustrated by comparing the mass yields at the lowest and highest conditions (8 vs 16) in Fig. 2a. For pine, the mass yield decreases from 91 % at test condition 8, to 60 % at test condition 16 (a difference of 31 %), while switchgrass decreases from 68 % to 46 % (a difference of 22 %) under the same test conditions. The mass yields indicate that molten salts more readily torrefy switchgrass compared to pine, wherein conditions that only mildly torrefy pine significantly torrefy switchgrass. However, due to the severity of torrefaction of switchgrass, even at the milder test conditions, switchgrass mass yields vary less between test conditions than pine.

Fig. 2b shows the sensitivities of the mass yields to the various process conditions where the effects represent a change in mass yield percentage points (%-points) per change in process condition level. For both feedstocks, the dominant process conditions influencing mass yields are temperature, residence time, and lithium content. However, the ranking of these three conditions depends on the feedstock. Pine is most influenced by temperature, with mass yields that are, on average, 11.4 %-points lower at 225 °C than at 200 °C. Increasing residence time has an effect of −8.5 %-points, and increasing lithium content has an effect of −6.5 %-points. In contrast, for switchgrass, the magnitude of the effects of these three variables are similar. Lithium content is most impactful with a −7.3 %-point effect while both temperature and residence time have slightly lower effects at −5 to −6 %-points. For both feedstocks, the salt-to-biomass ratio and sweep gas have little effect. The results show that the low salt content (15:1) can provide thorough contact between the salt and biomass, and the use of a reactive gas (air) is not significant, likely due to the increased difficulty for oxygen to diffuse through the molten salt bath to reach the biomass. This low sensitivity to sweep gas could impact the molten salt process at a larger scale because it indicates that an inert environment, which can be energetically and economically expensive, need not be maintained. For changing particle size, there is an insignificant effect on switchgrass, while pine has a slight sensitivity to it. However, the effect of particle size for pine is much lower than the more impactful variables of temperature, time, and lithium content. A possible reason for the low effect of particle size on mass yields for switchgrass may be due to the tendency for the switchgrass to reduce into thin, ribbon-like particles (Fig. 1). The thickness of the ribbon-like particles tends to be the smallest dimension, and does not change much between the particle size groups. Since the transportation of the salt through biomass is a function of the smallest dimension, the salt transportation is similar between the thin switchgrass particle size groups but different for the pine particle size groups. Additionally, herbaceous biomass is generally more porous and less dense than woody biomass (Mu et al., 2023), which may aid in salt penetration into the switchgrass.

3.2. *Chemical composition*

The chemical composition of the molten salt torrefied and raw pine and switchgrass samples are shown in Fig. 3. The hemicellulose fractions in Fig. 3 represent the xylan and arabinose content of the biomass, while the cellulose represents the glucan content. The Klason-lignin is comprised of the acid-insoluble residue in the biomass, and the portion labeled as “other” consists of unquantified components, including extractives, acid-soluble lignin, acid-soluble minerals, and trace amounts of water (Barta-Rajnai et al., 2016). Hereafter, the “other” component will be referred to as extractives. The mass losses of the samples are included in Fig. 3 to show the comprehensive decomposition of the torrefied biomass. Comparing the torrefied values to the raw values demonstrates that the molten salt treatment promotes the decomposition of holocellulose (cellulose and hemicellulose) and extractives while promoting an increase in lignin content for both feedstocks. This is seen by the loss or gain in percent weight of these components compared to the values for the raw biomass. Hemicellulose is the most decomposed component for both pine and switchgrass. The greater decomposition of the hemicellulose is expected due to its lower thermal stability compared to cellulose and lignin (Chen and Kuo, 2011; Faleeva et al., 2022). The raw dry pine and switchgrass initially have 15–16 % hemicellulose, which completely decomposes under the most severe test conditions, with two pine samples and seven switchgrass samples having less than 0.5 % hemicellulose remaining after molten salt torrefaction. The data shows that, although both feedstocks exhibit samples with complete decomposition of hemicellulose, switchgrass generally exhibits greater levels of hemicellulose decomposition than pine across the test conditions. For example, the least severely torrefied pine (test condition 8) retains 81 % of the raw hemicellulose content while the least severely torrefied switchgrass retains only 34 % of the raw hemicellulose content under the same test condition. The results demonstrate that the switchgrass hemicellulose is readily decomposed, almost completely, even under the least severe test conditions.

As for the cellulose, the raw pine has a higher cellulose content of 32.8 % compared to the 23.6 % in the raw switchgrass. Both feedstocks experience decomposition of cellulose from the molten salt treatment, although it never fully decomposes under the conditions tested. The average cellulose content of the torrefied pine is 25.5 % whereas the average cellulose content of the torrefied switchgrass is 14.9 %. Because of the higher inherent content of cellulose in pine, the pine, on average, has a larger absolute change in cellulose content than switchgrass from the molten salt treatment. However, switchgrass experiences a larger percent decrease of cellulose on average than pine relative to the initial cellulose. For instance, when considering the most severely torrefied samples in terms of cellulose decomposition (test condition 2), switchgrass only retains 27.5 % of the original cellulose whereas the pine retains 41.8 % of the original cellulose, under the same conditions. Furthermore, the least severely torrefied switchgrass sample in terms of cellulose decomposition (sample 8) retains only 73.6 % of the original cellulose. Meanwhile, the least severely torrefied pine samples in terms of cellulose decomposition (samples 13 and 3) are essentially equivalent to raw pine in terms of cellulose content. The cellulose compositions of both the most and least severely torrefied samples indicate that the switchgrass cellulose is more susceptible to degradation from the molten

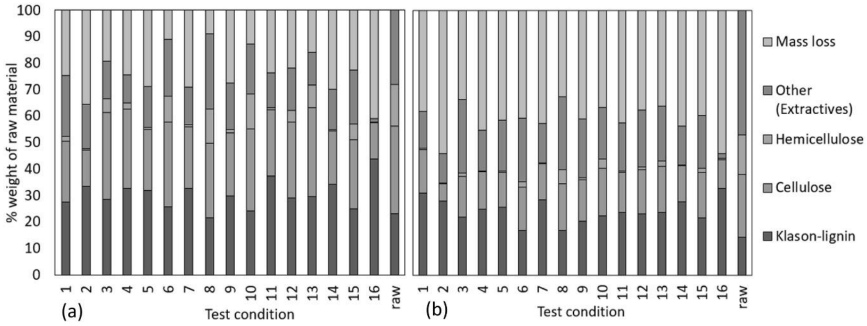


Fig. 3. Chemical composition of molten salt torrefied and raw biomass. (a) Pine, (b) switchgrass.

salt treatment than the pine cellulose. Furthermore, it is clear that the molten salt is responsible for this phenomenon when considering that, for inert gas torrefaction, the switchgrass cellulose withstands temperatures higher than that of pine cellulose (Fig. 4). Moreover, both feedstocks demonstrate substantial decomposition of cellulose from the molten salt treatment at temperatures below those needed to reach similar decomposition levels from inert gas torrefaction.

The extractives account for 27.9 % in raw pine and 46.9 % in raw switchgrass. After torrefying in the molten salts, both feedstocks experience a decrease in extractives, except for one pine sample remaining essentially the same in terms of extractives. Switchgrass experiences a much larger decomposition of extractives than pine, likely due to the larger inherent content of the less stable, highly volatile extractive compounds in herbaceous biomass than in woody biomass (Q. Wang et al., 2021). After torrefaction, both feedstocks contain similar amounts of stable extractives across the test conditions with minor deviations. The average extractive content of the torrefied pine is 16.2 %, while the average extractive content of the torrefied switchgrass is 18.3 %. Another notable trend for both feedstocks is the extensive decomposition of extractives resulting from the combination of the high process conditions levels of test condition 16. After torrefying under test condition 16, both pine and switchgrass have less than 2 % extractives remaining. These samples have the lowest extractive content. Meanwhile, the pine and switchgrass samples with the second lowest extractive content have, respectively, 10.6 % and 11.1 % extractives remaining. The data shows that, for both feedstocks, complete decomposition of extractives is not achieved unless all process condition levels are maximized.

For both pine and switchgrass, the lignin content increases from the raw content due to the molten salt treatment, except for one case. Raw pine has 23.3 % lignin content and raw switchgrass has 14.4 % lignin content. Under the torrefaction conditions leading to the most severely torrefied samples, the lignin content in pine increases by 88 % from the raw content, whereas the lignin content in switchgrass increases by 127 % from the raw content. The increase in lignin is due to the cross-linking and carbonization reactions of the holocellulose derivatives, which result in the formation of acid-insoluble, carbonaceous products often referred to as pseudo-lignin (Hu et al., 2012; Sannigrahi et al., 2011; Shinde et al., 2018). The inherent lignin content in woody biomass is higher than in herbaceous biomass. Because of this, all of the pine samples result in larger final lignin contents than the switchgrass samples except for the samples torrefied under test condition 1. However, the data shows that the holocellulose of switchgrass is more apt to carbonize into pseudo-lignin than the holocellulose of pine because there is a larger average absolute increase in lignin content for the switchgrass samples than for the pine samples.

Fig. 4 shows the chemical composition and mass loss of pine and switchgrass torrefied in inert gas over increasing temperatures. The torrefaction in inert gas reduces the holocellulose and extractives content while increasing the lignin content as temperatures increase. At torrefaction temperatures of both 240 and 280 °C, the uncertainty in the cellulose, hemicellulose, and lignin content for inert gas torrefied pine are ±1.24 %, ±1.11 %, and ±7.28 %, respectively. At torrefaction temperatures of both 260 and 300 °C, the uncertainty of the cellulose, hemicellulose, and lignin content for inert gas torrefied switchgrass are ±0.66 %, ±0.18 %, and ±5.40 %, respectively. Comparing Figs. 3 and 4 demonstrates that molten salt torrefaction provides equal to or greater decomposition of holocellulose and extractives than inert gas torrefaction, even at lower temperatures and residence times. An example of the superior performance of molten salt torrefaction is observed by comparing biomass torrefied under test condition 8 (Fig. 3) with biomass torrefied in inert gas at 200 °C (Fig. 4). The salt torrefied and inert gas torrefied samples were both torrefied at the same temperature of 200 °C. However, the salt torrefied samples were held at temperature for only 30 minutes, as opposed to the 2 h for the control samples. Even so, the salt treatment provides a significantly larger decomposition of extractives for switchgrass. Additionally, there is a greater decomposition of holocellulose and a greater increase in lignin for both feedstocks from the salt treatment versus the inert gas treatment. Looking at the more severely torrefied samples, the pine torrefied under test condition 16 has similar amounts of lignin to that of pine torrefied in inert gas at 280 °C, and similar amounts of holocellulose to that of pine torrefied in inert gas at 260 °C. Additionally, the lignocellulosic content of switchgrass torrefied under test condition 16 is comparable to that of switchgrass torrefied in inert gas at 280 °C. The results indicate that similar lignocellulosic compositions can be achieved by torrefaction in molten salts at temperatures 55 °C lower than what is required by torrefaction in inert gas. Furthermore, even at 320 °C, inert gas torrefaction is unable to decompose the extractives to less than 4 % for either feedstock, while molten salt torrefaction does so at 225 °C for both feedstocks. Thus, molten salts increase the severity of torrefaction compared to inert gas torrefaction, but also produce torrefied biomass with nuanced differences in the composition compared to inert gas torrefaction. These differences in composition, e.g. greater removal of extractives, may indicate that molten salt torrefaction uses reaction mechanisms unavailable to inert gas torrefaction.

Fig. 5 shows the main effects of the process conditions on the decomposition and/or formation of the lignocellulosic and extractive components of the molten salt torrefied biomass samples. The effects are in terms of a change in composition percentage points (%-points) per change in process condition level. Both feedstocks are most influenced by increasing torrefaction temperature and residence time, wherein the

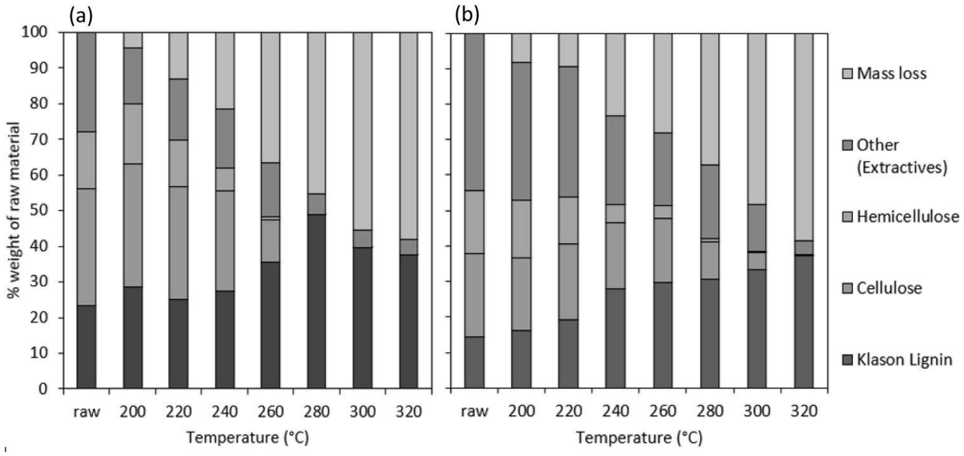


Fig. 4. Chemical composition of inert gas torrefied and raw biomass controls. (a) Pine, (b) switchgrass.

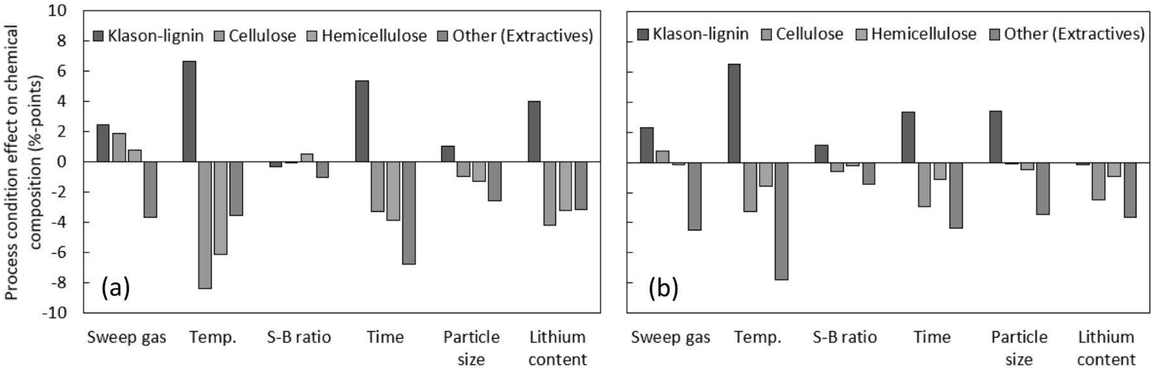


Fig. 5. Processing conditions effects on composition of torrefied (a) pine, (b) switchgrass.

largest increase in lignin and the largest decrease in holocellulose and extractives are a result of the increasing temperature and time. Increasing the temperature is the most prominent factor on the formation of lignin content for both feedstocks, with similar average increases in lignin of 6.6 % and 6.5 % for pine and switchgrass, respectively. The large formation of lignin by increasing temperature agrees with prior work that showed increasing temperature favors the cross-linking and carbonization reactions (Barta-Rajnai et al., 2016). For pine, increasing temperature results in substantially lower contents of cellulose (-8.4 %-points) and hemicellulose (-6.1 %-points), on average. Comparatively, for switchgrass, increasing temperature also results in lower contents of cellulose (-3.3 %-points) and hemicellulose (-1.6 %-points), but to a lesser degree than pine. The larger magnitude of the effect of temperature on the holocellulose of pine compared to switchgrass is likely due to the holocellulose of switchgrass being more susceptible to the molten salt catalysis than pine. The molten salt more readily breaks down the holocellulose of switchgrass at lower temperatures thus resulting in smaller effects when the temperature is increased. However, to achieve the same levels of catalytic effect for the pine holocellulose, the torrefaction system requires higher temperatures, which when implemented, result in increased decomposition and thus a greater temperature effect. Conversely, the decomposition of extractives in switchgrass compared to pine is shown to be more sensitive to the 25 °C increase in torrefaction temperature. An increase in temperature reduces the extractives content, on average, by −7.8 %-points in switchgrass and −3.6 %-points in pine.

For pine, increasing residence time results in an increase in the decomposition of hemicellulose and cellulose (-3.3 to −3.8 %-point effects). For switchgrass, the effect of increasing residence time results in a lower average hemicellulose decomposition than pine of −1.1 %-points and an average cellulose decomposition of −3 %-points, demonstrating the susceptibility of the herbaceous hemicellulose to degrade from the molten salt even at the shorter (30-minute) residence time. Increased residence time results in a large change in extractives for both feedstocks. Averaged across the test conditions, the extractives for pine and switchgrass are, respectively, −6.7 %-points and −4.3 %-points lower by increasing the residence time. Increasing the residence time by 90 minutes may play a role in the formation of pseudo-lignin for both feedstocks during molten salt torrefaction. Increasing residence time results in an increase in lignin for pine (5.4 %-point effect) and for switchgrass (3.3 %-point effect).

For switchgrass, decreasing the particle size from 710 to 850 μm to 250–500 μm results in a 3.4 %-point effect on the lignin content, similar in magnitude to the effect of increasing residence time. Additionally, decreasing the particle size is shown to decompose the switchgrass extractives by an average of −3.5 %-points. However, the decrease in particle size does not affect the hemicellulose and cellulose of switchgrass. For pine, similarly to switchgrass, reducing the particle size also results in the increase in lignin and decrease in extractives, but to a much lesser extent. Overall, decreasing the particle size exhibits little to no effects on the chemical composition of pine. Thus, reducing the particle size by half does not greatly affect the composition of pine, while the smaller particle size promotes lignin formation and extractive decomposition for switchgrass.

For pine, increasing lithium content by 10 % results in a moderate decomposition of holocellulose and extractives ~ (-3 to −4 %-point effects) and possibly the formation of lignin (4 %-point effect). However, for switchgrass, there is no lignin formation but mild decomposition of holocellulose and extractives ~ (-1 to −4 %-point effects) from increasing lithium. It is likely that the low lithium content readily cracks the holocellulose polymers in switchgrass, while the pine holocellulose requires the high lithium content to achieve more cracking. Thus, resulting in lower effects on the decomposition of cellulose and hemicellulose for switchgrass than pine. As for the effect of lithium content promoting the formation of lignin in pine while being impartial to the lignin in switchgrass, it could be that the higher lithium content indirectly partakes in the carbonization and cross-linking reactions more for pine than it does for switchgrass. Pseudo-lignin is produced through the heating of xylan and glucan, which are primarily derived from the decomposition of holocellulose (Xiao et al., 2007; Cheng et al., 2018). For switchgrass, the holocellulose is thoroughly cracked into xylan and glucan with the low lithium content making it accessible to undergo carbonization and cross-linking. Therefore, increasing lithium content yields little effect on further producing xylan and glucan to undergo carbonization because the hollocellulose has already broken down. Whereas for the pine holocellulose, being less susceptible to salt catalysis, it is not readily cracked into xylan and glucan with the low lithium content, thus requiring the high lithium content to expedite the xylan and glucan production to allow for carbonization and cross-linking into pseudo-lignin. Hence, by indirect means, the high lithium content is responsible for the increase of lignin in the woody pine biomass.

The effect of using an inert gas for molten salt torrefaction results in a decrease in extractives and a minor increase in lignin and cellulose for both pine and switchgrass. Hemicellulose does not significantly change for either feedstock due to sweep gas type. It is possible that, although mostly blocked by the salt, small amounts of reactive oxygen gas diffuse through the salt resulting in minor combustion of the stable carbon during torrefaction. By using an inert gas, the stable carbon is not combusted, therefore promoting Klason-lignin retention. For similar reasons, using inert gas promotes the retention of cellulose by preventing any combustion from the presence of air. However, using nitrogen compared to air results in a negative effect on extractives for both feedstocks. The salt-to-biomass ratio does not yield any significant effects on the lignocellulosic and extractive components of either feedstock. The insignificant effect of salt-to-biomass ratios on the chemical composition of pine and switchgrass reinforces the idea that so long as sufficient contact is maintained between the salt and biomass, the amount of salt can be reduced.

3.3. Higher heating value

Fig. 6 shows the higher heating values (HHV) of the salt torrefied and inert gas torrefied samples, as well as the main effects of the process conditions on HHV. Shown in Fig. 6a, both feedstocks increase in HHV from the molten salt treatment, which can be accredited to the increased relative lignin content. Lignin is the most energy dense lignocellulosic component followed by cellulose, then hemicellulose (Zhao et al., 2017). As a woody biomass, pine has a higher inherent lignin content than the herbaceous switchgrass. Therefore, the pine is generally seen to have higher HHV than switchgrass as shown in Fig. 6a. The HHV of the torrefied biomass increases from the raw biomass for both feedstocks except for two pine samples (test conditions 6 and 8) which were among the least severely torrefied samples. This decrease in HHV is likely due to loss of energy-dense, water-soluble compounds during washing of the biomass. Although there is likely a reduction in HHV from washing, the pine still reaches a HHV of 23.18 MJ/kg when torrefied under the highest condition levels (test condition 16). This increase in HHV of pine from test condition 16 provides an 18.23 % improvement from the HHV for raw pine (19.60 MJ/kg). The switchgrass torrefied at the highest condition levels (test condition 16) has a larger increase in HHV than pine, with a 23.93 % improvement from its raw counterpart (17.62–21.84 MJ/kg). Furthermore, the HHV of the least torrefied switchgrass (18.87 MJ/kg) is 7.1 % higher than the HHV of the raw switchgrass (17.62 MJ/kg). Meanwhile, pine had no increase in HHV under the same conditions. If the loss in HHV from the washing step is eliminated or reduced, it is possible that even greater increases in HHV would be achieved.

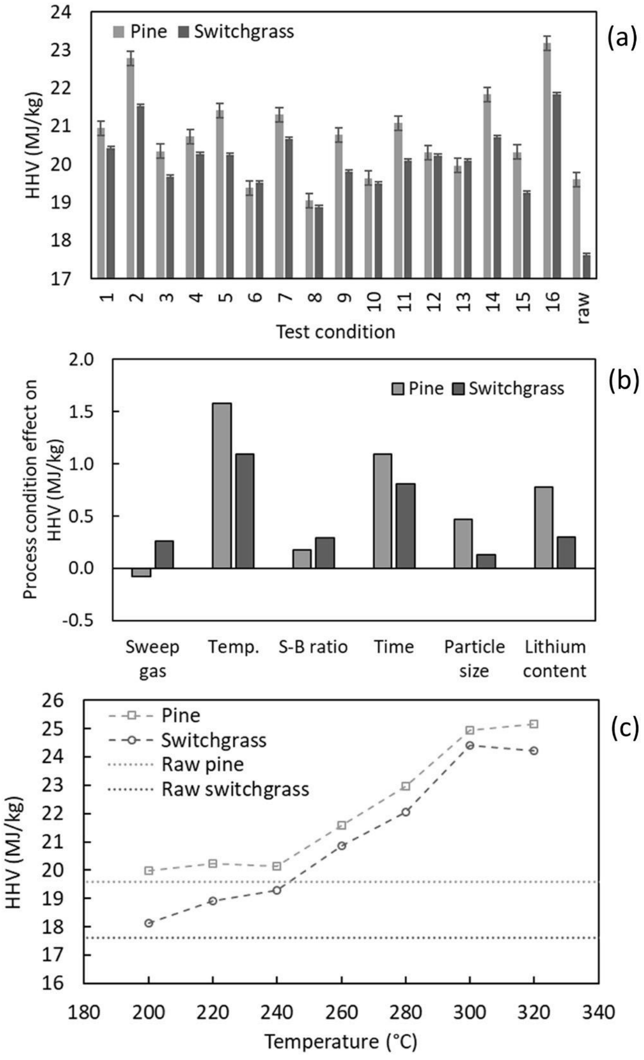


Fig. 6. Higher heating value and process condition effect on molten salt torrefaction. (a) Experimental pine and switchgrass (b) Effects of process conditions on higher heating value (c) Control pine and switchgrass.

The HHV data shows that the average improvement for switchgrass is greater than the average improvement for pine relative to their raw counterparts. In addition, torrefying under test conditions that result in lower severity of torrefaction effectively reduces the inherent disparity in the HHV between raw pine and raw switchgrass. For example, five test conditions resulted in torrefied pine and switchgrass with similar HHV even though the HHV of raw pine is initially 1.98 MJ/kg higher than that of raw switchgrass. However, as the torrefaction severity increases, the HHV of pine increases, eventually reaching a HHV that is 1.34 MJ/kg higher than the HHV of switchgrass torrefied under the same condition (test condition 16). This is because the pine begins to experience the physiochemical changes responsible for increased energy density at the high condition levels which occurred for switchgrass at the low condition levels. For both feedstocks, molten salt torrefaction yields a torrefied biomass with a greater HHV than inert gas torrefaction at the same temperature. Thus, lower processing temperatures can be used with molten salt torrefaction to produce similar levels of HHV as inert gas torrefaction. This is in agreement with prior work for molten salt torrefaction of pine (Backer and Gladen), but now demonstrates it for an herbaceous feedstock as well. Comparing Figs. 6a and 6c, the most severely molten salt torrefied samples for pine and switchgrass have similar HHVs to inert gas torrefied biomass at 280 °C. The molten salts are able to successfully reduce the torrefaction temperature by 55 °C while providing the same improvement in HHV. The uncertainty of the HHV for inert gas torrefied pine is ±0.25 MJ/kg and ±0.35 MJ/kg at 240 and 280 °C, respectively, and is ±0.22 MJ/kg and ±0.20 MJ/kg for switchgrass at 260 and 300 °C, respectively.

As for the effects of the process conditions on HHV, both feedstocks are heavily influenced by temperature and time in that order, with lithium content being the third most impactful, but to a lesser degree for switchgrass (Fig. 6b). Thus, molten salt torrefaction is similar to inert gas torrefaction in the regard that temperature and time are the dominant process conditions for increasing HHV. Temperature is the driving force for torrefaction, and residence time permits the thermochemical reactions to finalize. The positive effect of increasing lithium content on HHV is more obvious for pine than it is for switchgrass in that the effect of lithium content on pine is more than double that of the effect for switchgrass. Also, the effect of lithium content on switchgrass (0.3 MJ/kg) is comparable to the effects of sweep gas (0.27 MJ/kg) and salt-to-biomass ratio (0.3 MJ/kg) on switchgrass. In contrast, for pine, the effect of lithium content (0.78 MJ/kg) yields a greater effect than the sum of the effects of sweep gas, salt-to-biomass ratio and particle size. Increasing lithium content may have a low effect on switchgrass HHV because the low lithium content salt blend significantly decomposes the low energy dense cellulose and hemicellulose (Fig. 3b), resulting in higher relative lignin content, which helps drive higher HHV. Thus, increasing lithium content yields little benefit in further decomposing the holocellulose and increasing the HHV of switchgrass. Additionally, the high lithium content salt blend may promote the degradation of the higher energy density lignin in the switchgrass limiting the HHV ceiling at the high lithium content condition. These two factors, which are less influential on pine, would result in a smaller change in HHV between the low lithium and high lithium conditions for switchgrass. Changing the S-B ratio has a minor effect on both feedstocks, likely due to the tendency for the salt to have slightly more contact with the biomass from the increased salt content. The data indicates that the effect of sweep gas on HHV is even less prominent than the effect of the S-B ratio. Using an inert sweep gas increases HHV for switchgrass by 0.27 MJ/kg while reducing HHV for pine by −0.08 MJ/kg. The effects agree with inert gas torrefaction performed by (Huang et al., 2021), where herbaceous switchgrass is more vulnerable to the reactive air than the woody pine.

However, the magnitudes are much lower for the salt torrefaction than the inert gas torrefaction. The effect of particle size is minor on the HHV of switchgrass, with an effect of 0.14 MJ/kg, whereas for pine, the particle size has a more notable effect of 0.47 MJ/kg. This is likely due to reduced salt penetration into the pine particles which have a larger variability in their smallest dimension between particle size groups compared to that of switchgrass particles, and are generally denser and have a lower porosity. However, the effect of decreasing particle size of pine from 710 to 850 μm to 250–500 μm is only 30 % of the effect of increasing torrefaction temperature and less than 45 % of the effect from increasing residence time.

3.4. Total Carbon and Nitrogen Content

The torrefaction process increases the carbon content of the solid material with respect to the raw biomass (Fig. 7). The average carbon content for the torrefied biomass across all the experimental conditions is 53.8 % for pine and 50.9 % for switchgrass (Fig. 7a). The average carbon content of the salt torrefied pine is 6.5 %-points higher than the carbon content of raw pine, whereas the average carbon content of the salt torrefied switchgrass is 8.8 %-points higher than the carbon content for raw switchgrass. Carbon content is slightly higher for pine than switchgrass at every test condition besides 6. For test condition 16, salt torrefied pine reaches a maximum of 60.6 % total carbon, whereas switchgrass peaks at 54.9 % at the same test condition. Carbon contents for these high severity test conditions are similar to those of biomass torrefied in inert gas at 280ºC (Fig. 7c). As seen in Fig. 7b, total carbon content is most sensitive to temperature, followed by residence time and lithium content, for both feedstocks. In general, the carbon content sensitivities follow the same trends as those observed for HHV. Temperature increases carbon content with a 4.4 %-point effect for pine and a 2.8 %-point effect for switchgrass. Averaged across the test conditions, the pine carbon content increases by 3.0 %-points with residence time and by 1.8 %-points with lithium content, with slightly lower responses in switchgrass. Pine carbon content is more sensitive to these process conditions since changing temperature, residence time, and lithium content levels have a greater compositional effect on holocellulose in pine than in switchgrass, as discussed previously. As cellulose and hemicellulose degrade, relative carbon content increases due to the higher carbon mass ratio of lignin. Particle size is seen to have a slight effect on carbon content in pine (1.5 %-points). By comparison, switchgrass carbon content is minimally sensitive to particle size, likely for similar reasons as prior metrics. Inert sweep gas and a high S-B ratio have a minimal effect on carbonization for both feedstocks.

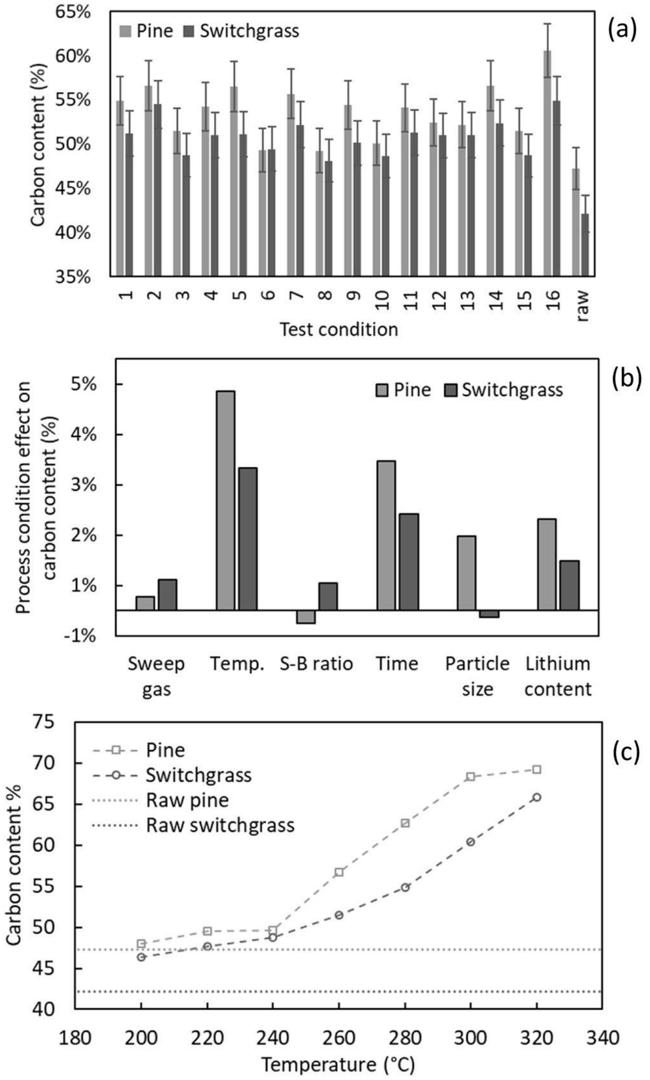


Fig. 7. Carbon content and process condition effects on biomass torrefaction. (a) Experimental pine and switchgrass (b) Effects of process conditions on nitrogen content (c) Control pine and switchgrass.

The molten salt torrefaction process increases the nitrogen content of raw biomass, which has low intrinsic values (Fig. 8). The average nitrogen content for salt torrefied pine across all test conditions was 0.42 %. In comparison, the average for switchgrass was 1.65 %, nearly four times greater than pine (Fig. 8a). Compared to raw, the nitrogen content for switchgrass increased by 0.60 %-points on average, and pine increased by 0.40 %-points. While the increase with respect to raw nitrogen content equates to a 57 % relative change for switchgrass, it is a 2100 % increase for pine. The higher percent increase for pine is due to its low nitrogen content in the raw form. Small quantities of residual nitrate from the torrefaction process, as well as the accumulation of nitrogen-rich lignin (Huang et al., 2019), are possible drivers of the large nitrogen increases with respect to raw content. For example, 0.045 g potassium nitrate per 100 g biochar would suffice to increase nitrogen content by 0.6 %-points. This change for molten salt torrefaction is substantial compared to inert gas torrefaction effects on nitrogen content which has a nitrogen content less than 0.1 % for all temperatures. The nitrogen content of molten salt torrefied biomass samples is significantly higher than the values obtained via inert gas torrefaction, supporting the hypothesis that the use of molten salts increase the nitrogen content (Fig. 8). For example, the nitrogen content of the low severity, test condition 8 is 0.14 % for pine and 1.10 % for switchgrass. These values exceed the nitrogen content of inert gas torrefied biomass at 320 ºC for pine, and 300 ºC for switchgrass. The data collected agrees with prior work where decreases of 0.3 %-points or less in nitrogen content are common in inert gas torrefaction for a variety of herbaceous and woody feedstocks (Lima et al., 2009; Tumuluru et al., 2021). In some cases, processing temperatures in excess of 500 °C are necessary to achieve an increase in the nitrogen content of woody biomass with inert gas thermochemical processing.

The sensitivity of nitrogen content to the process conditions is similar between feedstocks for most process conditions, except that switchgrass is more sensitive to S-B ratio and particle size than pine (Fig. 8b). Pine is most sensitive to temperature (0.28 %-points) and residence time (0.23 %-points). This ranking follows the ranking of process conditions influence on other torrefaction metrics. However, switchgrass is most sensitive to particle size (0.35 %-points), followed by temperature (0.33 %-points) and residence time (0.28 %-points). Switchgrass also demonstrates a moderate sensitivity to salt-biomass ratio (0.18 %-points) not observed in pine, possibly from greater nitrate deposition. Lignin content in switchgrass also demonstrates higher sensitivity to particle size and S-B ratio than in pine (Fig. 5), which may help to

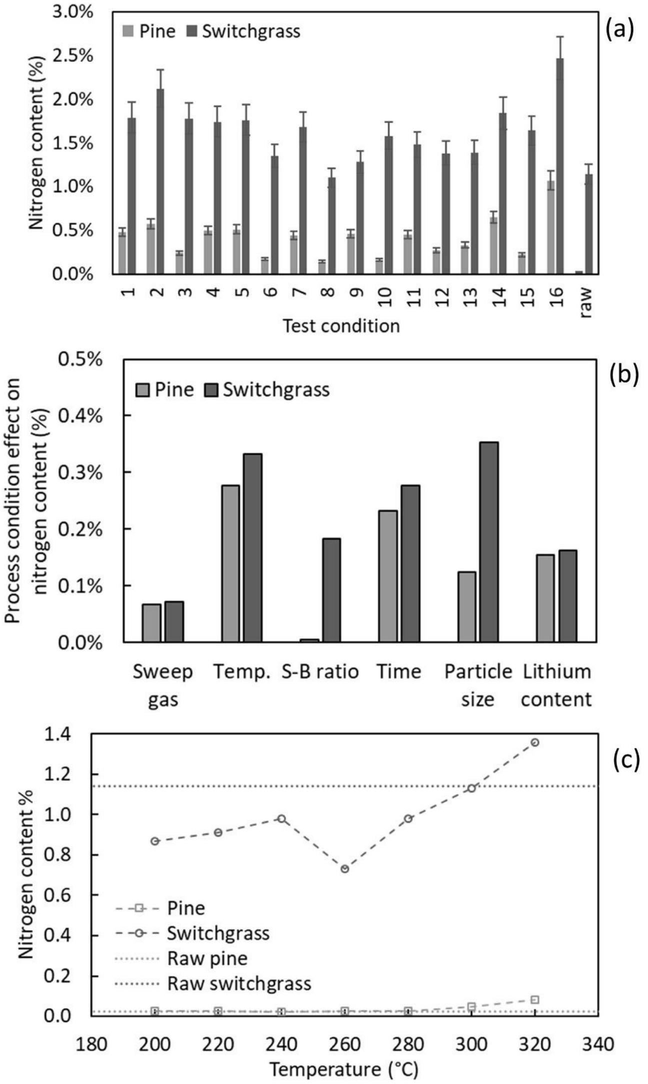


Fig. 8. Nitrogen content and process condition effects on biomass torrefaction. (a) Experimental pine and switchgrass (b) Effects of process conditions on nitrogen content (c) Control pine and switchgrass.

explain differences in nitrogen content. The lignin produced from grassy biomasses is known to contain nitrogen, while wood-based lignin typically contains no nitrogen (Huang et al., 2019). Thus, if the process results in a higher lignin content for switchgrass, the nitrogen content is expected to increase. However, pine lignin would not augment the sensitivity of nitrogen content to the process variables. Both pine and switchgrass are moderately sensitive to lithium content (0.16 %-points) and minimally sensitive to sweep gas (0.07 %-points).

3.5. pH

Molten salt torrefaction results in the neutralization of inherently acidic biomass (Fig. 9). The average pH of the biochar across the process conditions is 6.87 for pine and 7.17 for switchgrass (Fig. 9a). These average values represent an increase in pH of 2.45 for pine and 2.37 for switchgrass compared to the pH of the raw biomass. This neutralization is advantageous because it reduces any adverse effects of acidity in soil or fuel co-firing applications. It is most effective and economical to grow grain and grass cash crops in soils that are slightly acidic to slightly alkaline (Fernández and Hoeft, 2009). In contrast to molten salt torrefaction, pine does not neutralize with inert gas torrefaction (Fig. 9c), while for switchgrass, it takes temperatures over 260 °C to neutralize the biomass to a similar degree as molten salt torrefaction. The higher

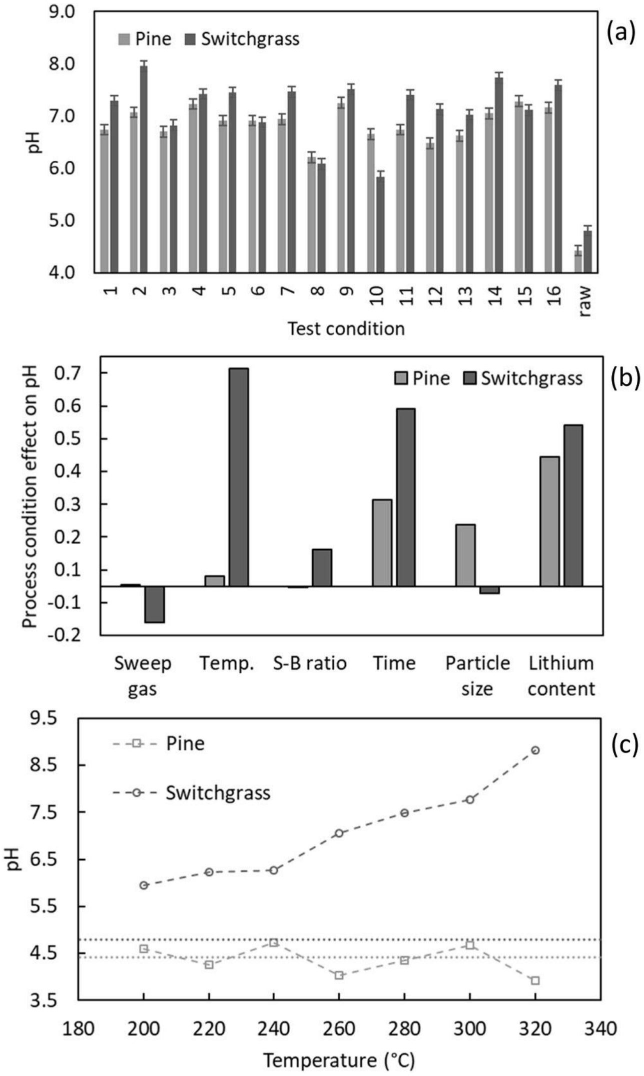


Fig. 9. pH and process condition effects on biomass torrefaction. (a) Experimental pine and switchgrass (b) Effects of process conditions on the pH (c) Control pine and switchgrass.

concentration of non-pyrolyzed, inorganic nutrients in switchgrass allows it to reach higher pH values than pine, as ash is produced from the biomass during torrefaction (Lima et al., 2009). This means that switchgrass biochar can also become alkaline at a lower temperature than pine, approaching a pH of 9 from 320 °C inert gas torrefaction (Fig. 9c). The uncertainty of the pH for inert gas torrefied pine at both 240 and 280 °C is ±0.168 and is ±0.135 for switchgrass at both 260 and 300 °C.

The combination of processing conditions can also significantly affect the pH of the resulting torrefied biomass. However, the pH of the resulting switchgrass biochar is more affected by the changing process condition levels than pine. Salt torrefied switchgrass pH values range from 5.84 to 7.95, whereas pine pH values only range from 6.21 to 7.28. As seen in Fig. 9b, the pH of switchgrass is affected most by temperature (0.67), followed by residence time (0.54), and lithium content (0.49), corresponding to the key variables affecting mass yield. Because high pH values in biochar are reliant on ash content, it is logical that the primary drivers of mass yield also

drive the pH higher (Lehmann et al., 2011). Sweep gas, S-B ratio, and particle size do not have a significant effect on the pH of switchgrass. The pH of pine shows the highest sensitivity to lithium content, with an effect of 0.40, followed by residence time (0.26). The temperature variable does not significantly affect the pH of pine, despite the relatively large increase in the pH with respect to raw pine. This is due to the relatively low ash content of pine lessening the dissolution of alkaline minerals. Molten salt torrefied pine is neutralized regardless, suggesting that the potential presence of residual neutral salts in the biochar have an effect on the pH of the product. The sweep gas and salt-biomass ratio variables have negligible effect on the pine pH.

3.6. *Water uptake*

Water uptake has both substantial positive and negative trends with the molten salt treatment (Fig. 10). The average water uptake across test conditions for salt torrefied pine is 11.1 g/g,

increasing from 7.5 g/g for raw pine (Fig. 10a). Average water uptake for switchgrass is 8.5 g/g, on par with 8.5 g/g for raw switchgrass. The water uptake ranges from 6.3 to 16.5 g/g for salt torrefied pine and 6.4–12.5 g/g for salt torrefied switchgrass. Pine is more responsive to increasing process condition levels, and exhibits a wider range of response in the water uptake experiment.

Low temperature torrefaction is known to increase hydrophobicity for a variety of biomass types, while at high temperatures, surface adsorption is increased through the decomposition of aliphatic compounds and generation of pyrogenic nanopores (Gray et al., 2014; Mao et al., 2019). Fig. 10c highlights these competing effects. For pine, water uptake mirrors lignin content in inert gas torrefied samples, as both peak at 280ºC (Fig. 4a). For temperatures under 240ºC, the dominating effect is reduced hygroscopicity following the removal of hydroxyl groups, slightly reducing moisture uptake (Tumuluru et al., 2021). An increase in water uptake as relative lignin content increases from 240 to 280 ºC indicates that nanopores are generated. Temperatures above

280 ºC result in increased brittleness and destroyed porous macrostructure, reducing the potential for water uptake. As seen in Fig. 10c, water uptake is higher for raw switchgrass than inert gas torrefied switchgrass. Initial torrefaction significantly reduces water uptake, which continues until a low point at 260 ºC, where a consistent buildup of lignin microstructure overcomes the hydrophobic effects present (Fig. 4b). This hypothesis is supported by noting the high structural integrity of switchgrass control samples, which remain in particle form after torrefaction at high temperatures, while pine particles begin to crumble into fine powder (Fig. 11) as lignin content increases under the same conditions. Conversely, molten salt torrefied switchgrass samples processed under severely torrefying test conditions did not retain structural integrity, while pine samples did. The robustness of microstructure in the two feedstocks is the primary driver for differences in water uptake. The uncertainty in water uptake for inert gas torrefied pine at both 240 and 280 °C is ±1.28 g/g and is ±0.814 g/g for switchgrass at both 260 and 300 °C.

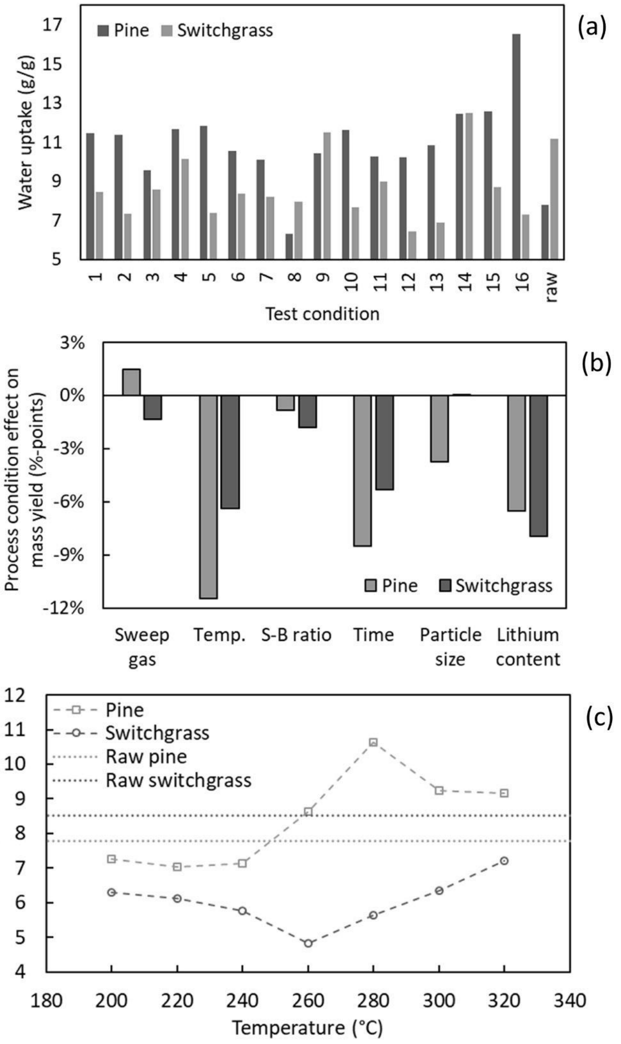


Fig. 10. Water uptake and process condition effects on biomass torrefaction. (a) Experimental pine and switchgrass (b) Effects of process conditions on water uptake (c) Control pine and switchgrass.

As seen in Fig. 10b, water uptake increases moderately with all process conditions for pine. Particle size has the most significant effect on pine (2.20 g/g), followed by lithium content (1.59 g/g). Although an essential driver of water uptake, the particle size variable refers to diameter before torrefaction and does not dictate particle size after torrefaction, which may have an effect of its own. Switchgrass water uptake is most affected by the S-B ratio, with a −1.54 g/g effect, demonstrating the feedstock's tendency to become highly brittle in a molten salt environment. Sweep gas and temperature have mild negative effects on switchgrass water uptake. Residence time, particle size, and lithium content have moderate positive effects, suggesting that while particle degradation may reduce water uptake, adsorption characteristics of switchgrass can still be optimized through the use of other process conditions.

Overall, molten salt torrefaction improves biomass for fuel and soil amendment end-uses. Mass yields decrease as the holocellulose and extractives decompose, although some holocellulose converts into pseudo-lignin. The increase in relative lignin content from the molten salt treatment, in turn, increases the energy density of the biomass. The improved HHV and increased lignin content correlate with the carbonization observed from the treatment, all of which are desirable for fuel applications. The nitrogen content increases from the molten salt treatment, possibly due to residual nitrate ion concentrations. Additionally, the pH of the acidic raw biomass increases from the treatment, especially as a result from increasing lithium content. The water uptake of pine dramatically improves as a response to all process conditions. Switchgrass has a split response to water uptake from the process conditions. Molten salt torrefaction of biomass develops a near neutral biochar wherein the pH can be adjusted depending on process conditions. Additionally, the biochar can retain trace nitrogen rich nitrate ions and can hold larger quantities of water than raw biomass, which may yield a superior soil amendment product.

The effect of the process conditions on the metrics mostly behaved as hypothesized wherein the high levels yield more severely torrefied biomass than the low levels. Similarly to inert gas torrefaction, the temperature and time process conditions are the most impactful on all metrics except for pH and water uptake. Lithium content is the third most impactful, likely due to the thorough polymer chain cracking that occurs at the low condition level. Particle size has minor impact and is generally insignificant. Sweep gas and S-B ratio have a minor impact on

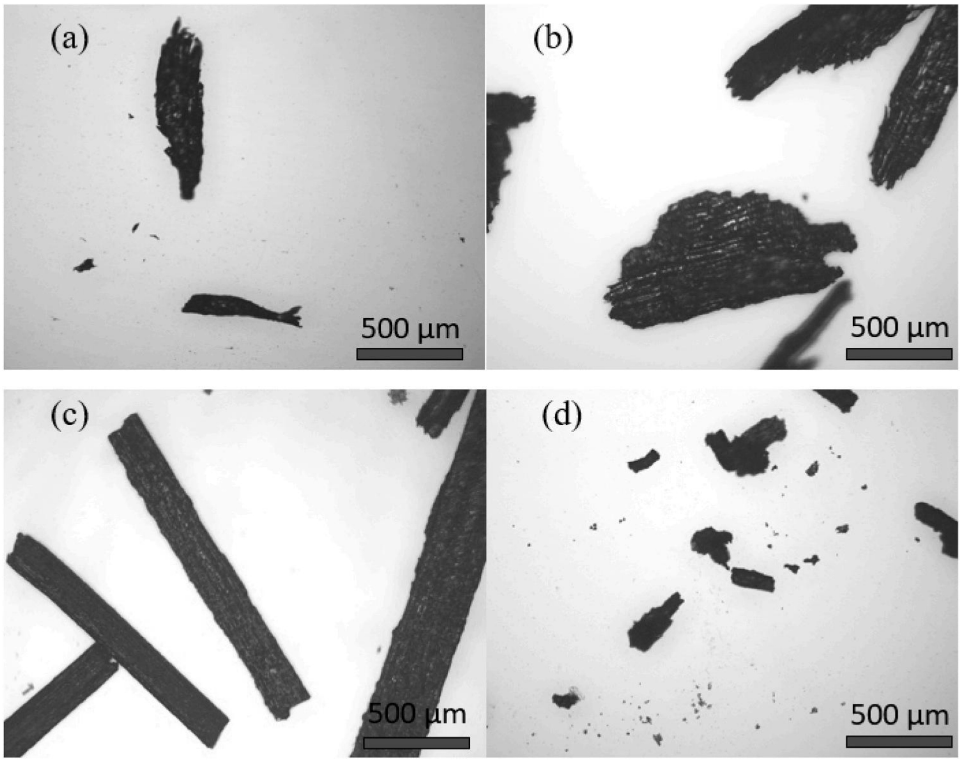


Fig. 11. Photographs of the highly torrefied feedstocks to illustrate particle integrity. (a) 320ºC inert gas torrefied pine exhibits dust particles, (b) test condition 16 pine, (c) 320ºC inert gas torrefied switchgrass, (d) test condition 16 switchgrass exhibits dust particles.

molten salt torrefaction.

Between the feedstocks, the pine is observed to have larger changes in metrics from the changes in process condition levels. A major reason for this outcome is due to the high amenability of switchgrass to the molten salt treatment. The reason for the difference in amenability is speculated to be related to the difference in physical nature between the woody pine and herbaceous switchgrass. The herbaceous switchgrass generally has weaker polymer structures, higher porosity, lower density, and has a higher surface area to volume ratio. These characteristics make the switchgrass more susceptible to the molten salt treatment.

4. Conclusions

This study explored the main effects of molten salt torrefaction process conditions on ponderosa pine and cave in rock switchgrass in binary molten salt blends of lithium and potassium nitrate using a Plackett-Burman screening analysis. The investigated process conditions include temperature, residence time, lithium content, particle size, sweep gas, and salt-to-biomass ratio.

Switchgrass is seen to more readily torrefy from molten salt torrefaction than pine, wherein the low process condition levels more severely torrefy switchgrass than pine. As a result, increasing the process condition levels for molten salt torrefaction elicits a greater change in severity of torrefaction for pine than it does for switchgrass. Furthermore, both feedstocks are more severely torrefied from molten salt torrefaction than inert gas torrefaction at the same temperature. However, the resulting torrefaction products can slightly differ between the two torrefaction methodologies. For example, the pH of both feedstocks is neutralized from molten salt torrefaction whereas with inert gas torrefaction, the pH of switchgrass is only neutralized at very high temperatures and the pine is not neutralized.

For most torrefaction metrics and for both feedstocks, the three most dominant process conditions are temperature, residence time, and lithium content in that order. Increasing the torrefaction temperature by 25 °C and the residence time by 90 minutes greatly increases lignin and carbon content and HHV for both pine and switchgrass. Increasing the lithium content by 10 % is also shown to improve the catalyzing reaction, resulting in reduced mass yields, improved energy density and increased pH. A likely reason for lithium content having a lower effect than temperature and time is due to the thorough cracking of the polymer chains even at the low lithium content level, especially for switchgrass.

Decreasing particle size by half has marginal to no effect on the metrics. Sweep gas and salt-to-biomass ratio have insignificant effects overall, some of which are an order of magnitude lower than the effects of temperature. This indicates that the tested conditions provide sufficient salt-to-biomass contact and prevent gaseous oxygen diffusion to the biomass. The low sensitivity to sweep gas and salt to biomass ratio could be impactful for molten salt torrefaction at a larger scale because it indicates that an inert environment, which can be energetically and economically expensive, need not be maintained. Additionally, lower salt-to-biomass ratios can be used so long as adequate contact between the two is maintained. Moreover, molten salt torrefaction provides highly torrefied solid biomass improving fuel and soil amendment end-uses.

CRediT authorship contribution statement

Adam C Gladen: Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Dilpreet S Bajwa:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization. **Lee Kohlin:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Hayden Pritchard:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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References

Backer, M.J., 2018. Experimental Investigation of Molten Salt Torrefaction and the Development of a Lab-Scale Torrefaction Methodology (Master's thesis, North Dakota State University).

Backer, M., Gladen, A., 2023. Impact of salt composition and temperature on low-temperature torrefaction of pine in molten nitrate salts. Energy 263, 126044. https://doi.org/10.1016/j.energy.2022.126044.

Barta-Rajnai, E., Jakab, E., Sebestyén, Z., May, Z., Barta, Z., Wang, L., Skreiberg, Ø., Grønli, M., Bozi, J., Czégény, Z., 2016. Comprehensive compositional study of torrefied wood and herbaceous materials by chemical analysis and thermoanalytical methods. Energy Fuels 30 (10), 8019–8030. https://doi.org/10.1021/acs.energyfuels.6b01030.

Beres, D.L., Hawkins, D.M., 2001. Plackett–Burman technique for sensitivity analysis of many-parametered models. Ecol. Model. 141 (1-3), 171–183. https://doi.org/10.1016/S0304-3800(01)00271-X.

Bergman, P.C., Boersma, A.R., Zwart, R.W.R., Kiel, J.H.A., 2005. Torrefaction for biomass co-firing in existing coal-fired power stations. ECN ECNC05013 Energy Res. Cent. Neth. 31.

Carveth, H.R., 1898. Studyof a three-component system. J. Phys. Chem. 2 (4), 209–228.

Chen, W.H., Kuo, P.C., 2011. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. Energy 36 (2), 803–811. https://doi.org/10.1016/j.energy.2010.12.036.

Cheng, B., Wang, X., Lin, Q., Zhang, X., Meng, L., Sun, R.C., Xin, F., Ren, J., 2018. New understandings of the relationship and initial formation mechanism for pseudo-lignin, humins, and acid-induced hydrothermal carbon. J. Agric. Food Chem. 66 (45), 11981–11989. https://doi.org/10.1021/acs.jafc.8b04754.

Edmunds, C.W., 2012. The effects of biochar amendment to soil on bio energy crop yield and biomass composition.(Master's thesis, The University of Tennessee Knoxville).

Faleeva, Y.M., Lavrenov, V.A., Zaichenko, V.M., 2022. Investigation of plant biomass two-stage pyrolysis based on three major components: cellulose, hemicellulose, and lignin. Biomass. Convers. Biorefin 169, 1–11. https://doi.org/10.1007/s13399-022-03385-1.

Gray, M., Johnson, M.G., Dragila, M.I., Kleber, M., 2014. Water uptake in biochars: The roles of porosity and hydrophobicity. Biomass. Bioenergy 61, 196–205. https://doi.org/10.1016/j.biombioe.2013.12.010.

Hathaway, B.J., Honda, M., Kittelson, D.B., Davidson, J.H., 2013. Steam gasification of plant biomass using molten carbonate salts. Energy 49, 211–217. https://doi.org/10.1016/j.energy.2012.11.006.

He, J., Zou, C., Zhou, X., Deng, Y., Li, X., Dong, L., Hu, H., 2022. Effects of Ca-compounds on the gases formation behavior during molten salts thermal treatment of bio-waste. Catalysts 12 (11), 1465. https://doi.org/10.3390/catal12111465.

Hu, F., Jung, S., Ragauskas, A., 2012. Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresour. Technol. 117, 7–12. https://doi.org/10.1016/j.biortech.2012.04.037.

Huang, S., Qin, J., He, Q., Wen, Y., Huang, S., Li, B., Hu, J., Zhou, N., Zhou, Z., 2021. Torrefied herb residues in nitrogen, air and oxygen atmosphere: thermal decomposition behavior and pyrolytic products characters. Bioresour. Technol. 342, 125991. https://doi.org/10.1016/j.biortech.2021.125991.

Huang, J., Fu, S., Gan, L. (Eds.), 2019. Structure and Characteristics of Lignin, 2019., in: Lignin Chemistry and Applications. Elsevier, pp. 25–50. https://doi.org/10.1016/B978-0-12-813941-7.00002-3.

Hunt, J., Duponte, M., Sato, D., Kawabata, A., 2010. The basics of biochar: a natural soil amendment. Soil Crop Manag. 30 (7), 1–6.

IEA (2023), Renewables share of totalenergy supply in the Net Zero Scenario, 2010-2030, IEA, Parishttps://www.iea.org/data-and-statistics/charts/renewables-share-of-total-energy-supply-in-the-net-zero-scenario-2010-2030-2,Licence: CC BY 4.0.

Fernández, F.G. and Hoeft, R.G.,2009. Managing soil pH and crop nutrients. Illinois agronomy handbook, 24,pp.91-112.

Jackson, R.B., Friedlingstein, P., Andrew, R.M., Canadell, J.G., Le Quéré, C., Peters, G.P., 2019. Persistent fossil fuel growth threatens the Paris Agreement and planetary health. Environ. Res. Lett. 14 (12), 121001 https://doi.org/10.1088/1748-9326/ab57b3.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota - a review. Soil Biol. Biochem 43 (9), 1812–1836. https://doi.org/10.1016/j.soilbio.2011.04.022.

Mao, J., Zhang, K., Chen, B., 2019. Linking hydrophobicity of biochar to the water repellency and water holding capacity of biochar-amended soil. Environ. Pollut. 253, 779–789. https://doi.org/10.1016/j.envpol.2019.07.051.

Mu, L., Wang, R., Xie, P., Li, Y., Huang, X., Yin, H., Dong, M., 2023. Comparative investigation on the pyrolysis of crop, woody, and herbaceous biomass: pyrolytic products, structural characteristics, and CO2 gasification. Fuel 335, 126940. https://doi.org/10.1016/j.fuel.2022.126940.

Nhuchhen, D.R., Basu, P., 2014. Experimental investigation of mildly pressurized torrefaction in air and nitrogen. Energy Fuels 28 (5), 3110–3121. https://doi.org/10.1021/ef4022202.

Niu, Y., Lv, Y., Lei, Y., Liu, S., Liang, Y., Wang, D., Hui, S., 2019. Biomass torrefaction: properties, applications, challenges, and economy. Renew. Sustain. Energy Rev. 115, 109395 https://doi.org/10.1016/j.rser.2019.109395.

Novak, J.M., Lima, I., Xing, B., Gaskin, J.W., Steiner, C., Das, K.C., Ahmedna, M., Rehrah, D., Watts, D.W., Busscher, W.J., Schomberg, H., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3, 195–206. https://www.researchgate.net/publication/38444634.

Nygård, H.S., Olsen, E., 2012. Review of thermal processing of biomass and waste in molten salts for production of renewable fuels and chemicals. Int. J. Low. Carbon Technol. 7, 318–324. https://doi.org/10.1093/ijlct/ctr045.

Peng, J.H., Bi, H.T., Sokhansanj, S., Lim, J.C., 2012. A study of particle size effect on biomass torrefaction and densification. Energy Fuels 26 (6), 3826–3839. https://doi.org/10.1021/ef3004027.

Phusunti, N., Phetwarotai, W., Tekasakul, S., 2018. Effects of torrefaction on physical properties, chemical composition and reactivity of microalgae. Korean J. Chem. Eng. 35, 503–510. https://doi.org/10.1007/s11814-017-0297-5.

Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., 2006. Torrefaction of wood. Part 2. Analysis of products. J. Anal. Appl. Pyrolysis 77 (1), 35–40. https://doi.org/10.1016/j.jaap.2006.01.001.

Repellin, V., Govin, A., Rolland, M., Guyonnet, R., 2010. Energy requirement for fine grinding of torrefied wood. Biomass. Bioenergy 34 (7), 923–930. https://doi.org/10.1016/j.biombioe.2010.01.039.

Sannigrahi, P., Kim, D.H., Jung, S., Ragauskas, A., 2011. Pseudo-lignin and pretreatment chemistry. Energy Environ. Sci. 4 (4), 1306–1310. https://doi.org/10.1039/c0ee00378f.

Shankar Tumuluru, J., Sokhansanj, S., Hess, J.R., Wright, C.T., Boardman, R.D., 2011. REVIEW: a review on biomass torrefaction process and product properties for energy applications. Ind. Biotechnol. 7 (5), 384–401. https://doi.org/10.1089/ind.2011.7.384.

Shinde, S.D., Meng, X., Kumar, R., Ragauskas, A.J., 2018. Recent advances in understanding the pseudo-lignin formation in a lignocellulosic biorefinery. Green. Chem. 20 (10), 2192–2205. https://doi.org/10.1039/c8gc00353j.

Singh, B., Singh, B.P., Cowie, A.L., 2010. Characterisation and evaluation of biochars for their application as a soil amendment. Soil Res. 48 (7), 516–525. https://doi.org/10.1071/SR10058.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2008. National Renewable Energy Laboratory. Determ. Struct. Carbohydr. Lignin Biomass. 17. NREL/TP-510-42618.

Strandberg, M., Olofsson, I., Pommer, L., Wiklund-Lindström, S., Åberg, K., Nordin, A., 2015. Effects of temperature and residence time on continuous torrefaction of spruce wood. Fuel Process. Technol. 134, 387–398. https://doi.org/10.1016/j.fuproc.2015.02.021.

Trubetskaya, A., Grams, J., Leahy, J.J., Johnson, R., Gallagher, P., Monaghan, R.F.D., Kwapinska, M., 2020. The effect of particle size, temperature and residence time on the yields and reactivity of olive stones from torrefaction. Renew. Energy 160, 998–1011. https://doi.org/10.1016/j.renene.2020.06.136.

Tumuluru, J.S., Ghiasi, B., Soelberg, N.R., Sokhansanj, S., 2021. Biomass torrefaction process, product properties, reactor types, and moving bed reactor design concepts. Front Energy Res 9, 728140. https://doi.org/10.3389/fenrg.2021.728140.

Wang, Q., Sun, S., Zhang, X., Liu, H., Sun, B., Guo, S., 2021. Influence of air oxidative and non-oxidative torrefaction on the chemical properties of corn stalk. Bioresour. Technol. 332, 125120. https://doi.org/10.1016/j.biortech.2021.125120.

Wang, H., Zhang, F., Li, L., Yu, H., Tu, R., Jia, Z., Jiang, E., Xu, X., 2021. Influence of molten salt torrefaction pretreatment on upgrading of bio-oil from camellia oleifera shell. SSRN Electron. J. https://doi.org/10.2139/ssrn.3899840.

Xiao, Y., Chung, T.S., Guan, H.M., Guiver, M.D., 2007. Synthesis, cross-linking and carbonization of co-polyimides containing internal acetylene units for gas separation. J. Membr. Sci. 302 (1-2), 254–264. https://doi.org/10.1016/j.memsci.2007.06.068.

Yang, Y., Hu, H., Yang, F., Tang, H., Liu, H., Yi, B., Li, X., Yao, H., 2020. Thermochemical conversion of lignocellulosic bio-waste via fast pyrolysis in molten salts. Fuel 278, 118228. https://doi.org/10.1016/j.fuel.2020.118228.

Yang, Y., Wang, T., Zou, C., Xu, K., Hu, H., Gao, L., Li, X., Yao, H., 2022. Comparing the thermal conversion behavior of bio-wastes in three molten nitrates. Renew. Energy 196, 617–624. https://doi.org/10.1016/j.renene.2022.06.123.

Zhao, C., Jiang, E., Chen, A., 2017. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. J. Energy Inst. 90 (6), 902–913. https://doi.org/10.1016/j.joei.2016.08.004.