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Impact of Pretreatment on Hydrothermally Carbonized Spruce

Anna Partridge, Ekaterina Sermyagina * and Esa Vakkilainen

Energy Technology, Laboratory of Sustainable Energy Systems, LUT University, PL 20, 53851 Lappeenranta, Finland; ahpartridge13@gmail.com (A.P.); esa.vakkilainen@lut.fi (E.V.)
* Correspondence: ekaterina.sermyagina@lut.fi; Tel.: +358-46-953-9001

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Abstract: Upgrading biomass waste streams can improve economics in wood industries by adding value to the process. This work considers use of a hydrothermal carbonization (HTC) process for the residual feedstock after lignin and hemicelluloses extraction. Batch experiments were performed at 200–240 °C temperatures and three hours residence time with an 8:1 biomass to water ratio for two feedstocks: Raw spruce and spruce after lignin extraction. The proximate analysis and heating value showed similar results for both feedstocks, indicating that the thermochemical conversion is not impacted by the removal of lignin and hemicelluloses; the pretreatment processing slightly increases the heating value of the treated feedstock, but the HTC conversion process produces a consistent upgrading trend for both the treated and untreated feedstocks. The energy yield was 9.7 percentage points higher for the treated wood on average across the range temperatures due to the higher mass yield in the treated experiments. The energy densification ratio and the mass yield were strongly correlated with reaction temperature, while the energy yield was not. Lignocellulosic composition of the solid HTC product is mainly affected by HTC treatment, the effect of lignin extraction is negligible.

Keywords: hydrothermal carbonization; lignin; biomass; energy densification

1. Introduction

Alternative fuel sources and low-carbon energy generation technologies are essential for meeting the future world energy needs [1]. Biomass waste streams from biorefineries can provide an alternative to fossil fuel resources if utilized efficiently [2]. In wood-based industries, such as pulp and paper, upgrading waste streams from primary production offers not only an additional revenue source, but also an opportunity for meeting internal heat and electricity demands for the industrial processes.

As the market develops for synthetic chemicals produced from biomass, new challenges and opportunities arise for wood-based industry. In industries such as pulp and paper, upgrading waste streams from primary production offers not only an additional revenue source, but also an opportunity for meeting internal heat and electricity demands for the industrial processes. One of the main components of wood is lignin, which comprises 18–35% of wood's dry mass, depending on the type of wood [3]. Lignin can be used to produce various chemicals and materials which are currently produced from expensive and non-renewable substances [4–6]. Chemicals which can be produced through biologic means include: vanillic acid, syringyl alcohol, ferulic acid and protocatehuic acid [7]. Additionally, petrochemical materials can be substituted in the production of emulsifiers, dyes, synthetic floorings, sequestering, binding, thermosets, dispersal agents, paints and fuels to treatments for roadways [8]. Hemicelluloses are also recognized as a potential material for various applications: Coating and packaging films [9], hydrogels [10], food emulsion stabilizers [11], etc.

The solid residue after the extraction process contains the considerable energy stored in the residual lignocellulosic fractions [12]. Energy uses for the treated wood include pelletization and combustion for the production of heat and power, reducing fossil fuel dependence in the energy system. However, the treated wood, like raw biomass, is heterogeneous, high in alkali metals, hydrophilic and has low energy density and bulk density [13]. One way to improve the combustion, handling and storage characteristics is through thermochemical upgrading. There are different processes for thermal upgrading of biomass, of which torrefaction and hydrothermal carbonization (HTC) produce primarily solid products with significantly improved handling characteristics and energy content [14,15].

In HTC process, the feedstock is reacted in a pressurized reactor vessel in the presence of water at moderate temperatures. The temperature is generally in the range of 180–250 °C with the maximum possible temperature being the critical temperature of water, 373 °C [15–18]. Pressure in the reactor is the saturation pressure of the water at the given temperature due to the closed nature of the reactor vessel. Residence time in the reactor can range from minutes to hours [16]. The main product of the HTC reactions is solid product (hydrochar), while byproducts include both aqueous liquid compounds (HTC liquor) and gaseous streams. Between 20%–70% of the minerals and inorganic compounds found in biomass ash are precipitated in the liquid byproduct stream [13,19] while the gaseous stream is approximately 90% CO_2 [14]. The aqueous HTC products are potential to produce certain high-value chemicals (furfurals, fatty acids, etc.) that can improve the overall performance of the HTC process [20,21].

HTC is favorable for wet feedstocks, eliminating the need for energy intensive drying processes [22,23]. The upgraded product has an increased carbon content [16], and improved handling and storage characteristics including increased homogeneity, improved grindability and hydrophobicity [16,24,25]. Reduced alkali and earth metals in hydrochar can reduce slagging and fouling problems caused by biomass combustion in heat and power applications [13,25]. In addition. this process can become a potential solution for some problematic biowastes (e.g., sludges and wastewaters) [23,26].

Previous studies have undertaken characterizations of lignocellulosic biomass [13,24,27–29], as well as chemical components of wood (hemicellulose, cellulose and lignin) individually [30–33]. The differences between hydrochar properties from HTC of raw wood—and wood with lignin and hemicelluloses removed—have yet to be reported in the literature. Determining the value of biomass waste after lignin and hemicelluloses extraction can provide insights into the economic feasibility of both the extraction and HTC processes. This study aims to quantify and assess the differences in energy yield, mass yield and chemical composition for untreated and treated hydrochars produced under the same reactor conditions. Experiments were undertaken at three different temperature conditions and a constant residence time and water to biomass ratio.

2. Materials and Methods

2.1. Materials

Spruce sawdust (waste stream) from sawmill operations was used as a feedstock for the HTC experiments. In addition to raw spruce sawdust (henceforth ‘untreated wood’), the spruce sawdust with hemicelluloses and lignin partially removed in a previous extraction treatment was used (henceforth ‘treated wood’). The extraction was performed using pressurized hot water extraction (180 °C for 120 min) to isolate hemicelluloses and lignin from the feedstock in a prior study [12]. The extraction equipment is described in detail by Kilpeläinen et al. [34].

2.2. Instrumentation

The experiments were carried out in a closed, stainless steel tube reactor at LUT University, Finland. The batch reactor (1 L inner volume and the dimensions of 705 mm in height and 42 mm inner diameter) has a flange connection at the top and screw cap at the bottom (Figure 1). Two NiCr–Ni (type K) thermocouples monitored the internal temperature (245 mm and 645 mm from the top, respectively), while an additional NiCr–Ni (type K) thermocouple monitored the external surface temperature of the reactor. The permitted deviation of the temperature measurement was ± 1.5 °C maximum according to the standard DIN EN 60584–2. The pressure inside the reactor was measured with the pressure transmitter (WIKA, model A-10, 0 ... 40 bar gauge) with the accuracy ≤ ± 0.5% of span. For safety purposes, the experimental unit also includes a pressure relief valve (set point pressure 40 bar, maximum temperature 300 °C). Heat was provided to the reactor by a thyristor-controlled electric resistance heating jacket. The required temperature level inside the reactor was maintained with a PID controller by varying the heat supply to the reactor. The experimental unit was covered by a thick insulation layer and an outer steel sheet. Data from the temperature and pressure sensors was recorded automatically every 3 s.

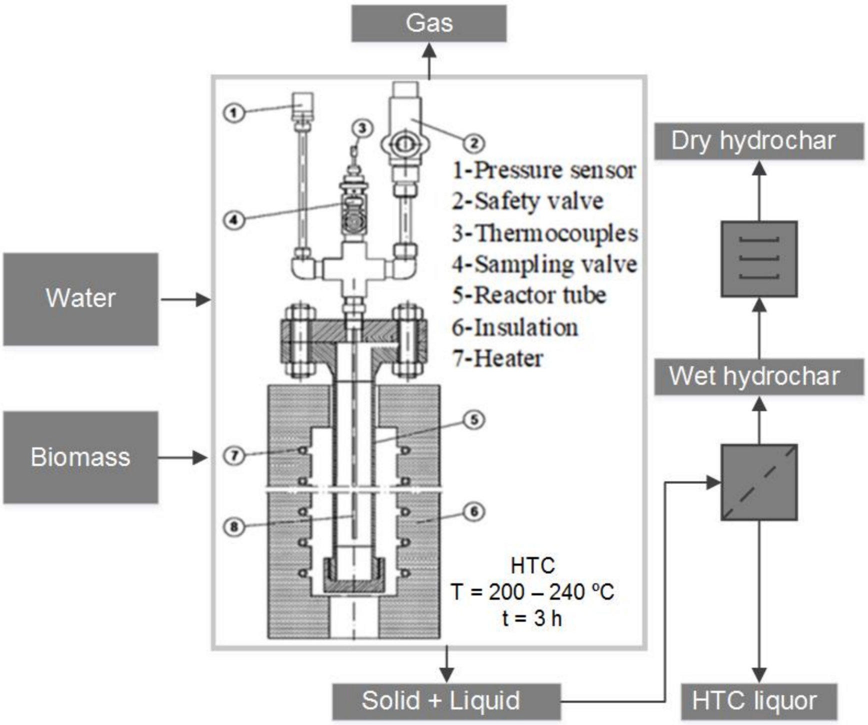

Figure 1. Hydrothermal carbonization (HTC) experimental unit and experimental procedure.

2.3. Methods

In the current study, three experimental conditions were analyzed for both the treated and untreated wood feedstocks with the same methodology as in work of Sermyagina et al. [27]. Residence time was held constant at 3 h and water to biomass ratio was maintained at 8:1 (30 g of feedstock and 240 mL of water). The temperature set points were varied between 200 °C, 220 °C and 240 °C. At the start of each experiment, the pre-weighed biomass sample and water were manually stirred. After the HTC process, the carbonized wood and liquid products were collected and subsequently separated by vacuum filtration using a Büchner funnel with Whatman glass microfiber filter study (grade GF/A). The solid product was then oven-dried overnight at a temperature of 105 ± 2 °C. All tests were performed twice or three times, and mass and energy yields were calculated using the average values of the sample properties.

Both the feedstock and the hydrochar products were characterized using standard procedures for heating value and proximate analysis. Similar hydrochars were mixed in order to provide a representative sample of the carbonized product from multiple runs. Characterization was performed at least twice for each reaction condition, and the average value is reported. The ash content of the solid product was determined according to the standard SFS EN 14,775 [35], using the mass of the inorganic residual after heating the biomass in air under controlled time and temperature conditions (550 °C at the maximum). Volatile matter was determined by measuring mass lost after seven minutes at a continuous temperature of 900 ± 10 °C as described by SFS EN 15148 [36]. The moisture content was measured using the moisture analyzer Sartorius 7093. The higher heating value was measured after grinding and pelletizing with the Parr 6400 calorimeter following standard SFS-EN 14,918 [37].

The chemical composition of the samples was evaluated in accordance with standard procedures. The milled samples were extracted successively with ethanol/toluene (1:2 *v/v*) (5 h), ethanol (4 h) and finally water (1 h), following the TAPPI method T264 cm-97 [38]. The extracted sample (extractive-free sawdust) was conditioned in a temperature and relative humidity (RH) controlled room (23 ± 1 °C, 50% ± 2% RH) until an equilibrium moisture was achieved. The extractions were carried out in duplicate, and the extraction yields were expressed in percentages in relation to the feedstock dry weight. For the extractive-free biomass, acid insoluble lignin and acid soluble lignin were determined according to the TAPPI T 222 om-11 [39] standard procedure. The content of holocellulose was calculated by difference.

3. Results and Discussion

3.1. Mass and Energy Yields

The unitless mass yield for each reaction, Y m, is calculated on a dry basis (d.b.) as

$$\text{Y m} = \text{m out}/\text{m in} \tag{1}$$

where: m in—initial mass of solids in the feedstock (d.b.), g; m out—the solid mass output (d.b.), g.

For both the HTC experiments with treated wood and untreated wood, the mass yield decreases as temperature increases. The main reaction mechanisms which degrade the solid feedstock in HTC are dehydration which removes hydroxyl groups; decarboxylation which removes carboxyl and carbonyl groups; and hydrolysis which cleaves ester and ether bonds [40]. Additional reaction mechanisms are polymerization and aromatization [41]. The hemicellulose in the biomass feedstock begins to degrade at the lowest temperature, already showing signs of hydrolysis at 180 °C [36]. In the range of 200–230 °C the cellulose goes through the hydrolysis reactions, and at temperatures between 220–260 °C lignin begins to degrade as well [40].

Mass yield at each reaction temperature is shown in Figure 2. Both individual runs at each temperature, and their average values are shown, with a linear regression fitted to the individual trial data. Notably, in the experimental results, the mass yield for the treated wood is higher than the mass yield for the untreated wood at each temperature. The difference is even more pronounced at the lowest temperature level. Such behavior can be explained by the effect of the prior extraction on the cellulose and hemicellulose fractions. This low temperature process modified the structure of the initial feedstock by preferentially removing the hemicelluloses while also extracting the lignin and degrading other components through hydrolysis.

Linear regressions were fitted to the individual run data for both treated and untreated wood using RStudio. The linear regression model for the treated wood appears to fit the data well, with $R^2 = 0.93$, while the correlation for the untreated wood experiments gives a 0.88 R^2 value. The equations for the correlations between reaction temperature, T, in °C, and fractional mass yield are given in Equations (2) and (3) for treated wood and untreated wood experiments, respectively.

$$\text{Y m, treated} = 1.54 - 0.00387\ \text{T} \tag{2}$$

$$\text{Y m, untreated} = 1.19 - 0.00265\ \text{T} \tag{3}$$

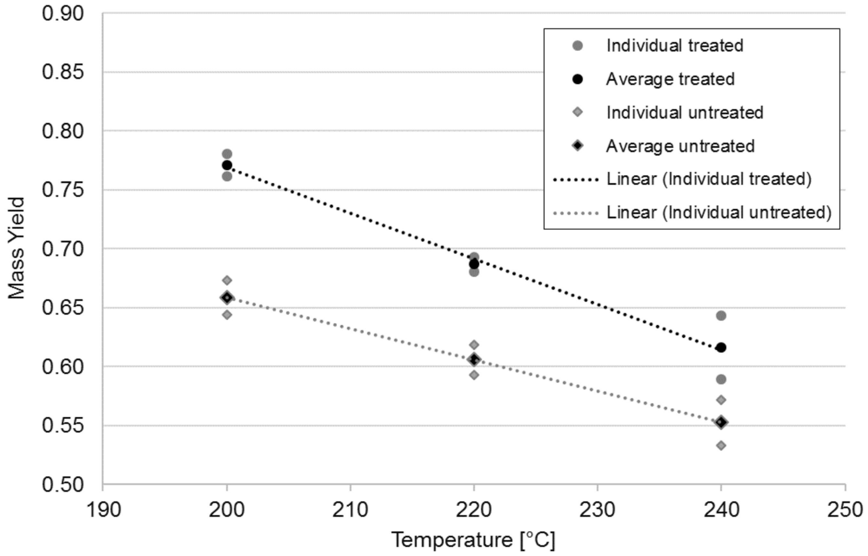

Figure 2. Mass yield of hydrothermal carbonization (HTC) experiments as a function of temperature for untreated and treated wood.

For the experiments with treated wood, the slope suggests that for each degree of temperature increase, the mass yield decreases by 0.39 percentage points. In case of the untreated wood, the HTC products reduce in mass yield less rapidly, with only a 0.27 percentage point change for each degree of temperature increase. A 95% confidence interval for the slope of each line was calculated using the *stats* package in RStudio to assess the significance of these differences. Because the measurements and tests were only conducted in duplicates or triplicates due to the lengthy experimental methods, it is not possible to determine the statistical distribution of the data points. The statistical analyses were therefore performed assuming a normally distributed sample set. The confidence intervals for the regression slopes overlap, and the slopes of both lines fall within each confidence interval range, as shown in Table 1. This indicates that the initial extraction process does not have a significant impact on the correlation between mass yield and reactor temperature during the HTC upgrading process.

Table 1. Confidence intervals for mass yield correlation coefficient with reaction temperature.

Samples	Slope	Lower Bound	Upper Bound
treated	−0.00387	−0.00534	−0.00239
untreated	−0.00265	−0.00399	−0.00131

The higher heating value of the feedstocks and the hydrochars for each temperature are shown in Figure 3. The higher heating value increased with increased reaction temperature, and the treated wood hydrochars showed a higher HHV across all runs. The increase in energy density with reaction temperature is due to the decrease in atomic O/C and H/C ratios resulting from the HTC reactions [12]. Both the untreated and treated wood have calorific values in the range of bituminous coal, while at reaction temperatures above 220 °C, the hydrochar is more comparable to hard coal. The values for the coal are from Donahue & Rais [42].

Lignin extracted from spruce by organosolv processes is reported by Gordobil et al. [43] to have a higher HHV than the raw feedstock used in these experiments, with an average value of 24.1 MJ/kg, compared to the 20.77 MJ/kg for untreated feedstock in this study. This would suggest that if lignin alone were removed, the treated wood feedstock should have a lower energy density than the raw wood. However, the treated wood has a higher energy content at 21.60 MJ/kg. Because the energy content is higher for treated wood hydrochars than their untreated counterparts at all temperature levels, it is clear that during the extraction process, chemical changes are occurring that also substantially reduce the hemicelluloses in the feedstock, and therefore impact the reaction severity. Further work is needed to determine if the extraction process produces similar chemical reactions to those that occur at low temperature (180 °C) in the HTC reactor, which could indicate a redundancy in the processing of the treated wood.

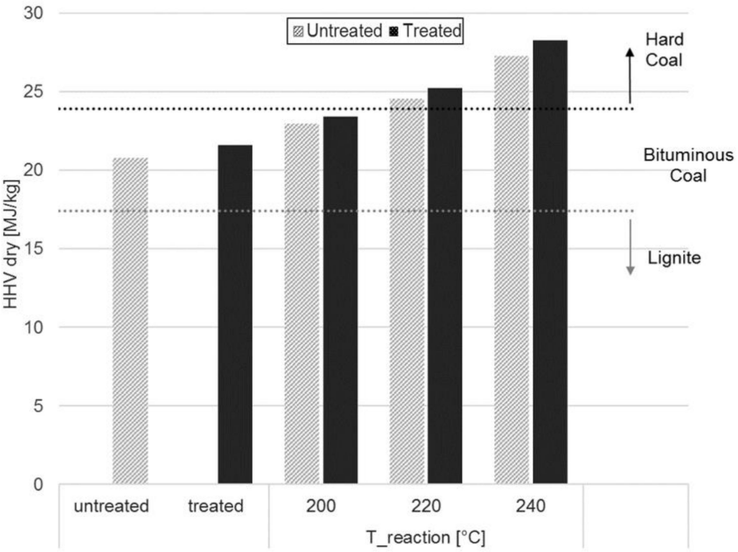

Figure 3. Higher heating value of hydrothermal carbonization experiments as a function of reaction temperature for untreated wood and treated wood.

Energy densification is an important quantity for comparing pretreatment processes, as it measures the upgrade in energy density from the raw feedstock. The energy densification ratio, ER, is calculated by Equation (4).

$$\text{ER} = \text{HHV prod}/\text{HHV fs} \tag{4}$$

where: HHV prod—higher heating value of the hydrochar, MJ/kg; HHV fs—higher heating value of the feedstock, MJ/kg.

The energy yield of each test is a measure of how much of the total energy content of the biomass feedstock is converted to solid hydrochar product on a dry basis. The solid energy yield, Ye, also a unitless fraction, is calculated as

$$\text{Ye} = \text{Y m} \times \text{HHV prod}/\text{HHV fs} \tag{5}$$

Energy densification ratio as a function of reaction temperature for the untreated wood and treated wood is shown in Figure 4 along with the energy yield.

As seen in Figure 2 the mass yield decreases with increasing temperature. However, the ratio of higher heating values, ER, increases with increasing temperature. The energy densification factor ranged from 1.1 to 1.3 for both feedstocks, strongly correlating with reactor temperature. The linear regression models for energy densification factor as a function of temperature are given in Equations (6) and (7) for treated and untreated feedstocks, respectively.

$$\text{ER tr} = 0.00567\ \text{T} - 0.0501 \tag{6}$$

$$\text{ER untr} = 0.0052\ \text{T} + 0.0574 \tag{7}$$

Statistical analysis of the coefficients in the linear regression was undertaken to assess the significance of the differences between the coefficients in Equations (6) and (7). The regression coefficients for the reactor temperatures are very similar for both feedstocks, and the 95% confidence intervals for these coefficients overlap, indicating the values are not statistically significantly different.

The reactor temperature explains 98% of the variation in the energy densification data for both feedstocks ($R^2_{treated} = 0.979$ and $R^2_{untreated} = 0.975$).

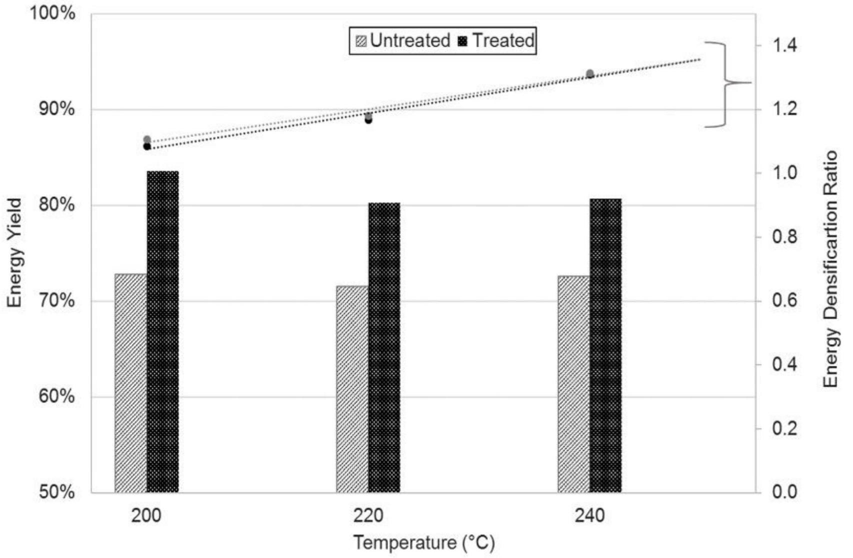

Figure 4. Energy yield and energy densification ratio of hydrothermal carbonization experiments as a function of reaction temperature for untreated and treated wood. Energy yield as bars is shown on left axis, while points and trendline show energy densification on right axis.

A linear regression between energy yield and temperature, however, explains only 64% of the variation in the treated wood hydrochar data and just 3% of the untreated wood hydrochar variation. Both 95% confidence intervals include zero, indicating that the hypothesis of a non-zero correlation is rejected, and therefore the energy yield is not likely to be impacted by changing reactor temperature. This lack of variation in energy yield with HTC temperature matches that found in previous batch HTC experiments [14]. A wider range of energy yields and correlation coefficients was seen across lignocellulosic biomass experiments reviewed by Bach & Skreiberg [25], likely differing from these experiments due to the specific feedstock type and the narrow reaction conditions in the current study. Both components of energy yield, Y m and the ratio of higher heating values, ER, were shown to have strong linear correlations with temperature, suggesting that Ye could alternatively be a nonlinear function of temperature.

Across temperature levels, the treated wood hydrochar yielded an average of 81.5% of the energy in the feedstock, whereas the untreated wood hydrochar yielded 71.8% on average. From this data, the treated feedstock appears to be substantially better in terms of the energy efficiency of the HTC process. Given that the energy densities of the HTC products are similar at each temperature, the average energy yield difference of nearly 10% between the untreated and treated wood indicates the treated wood responds more favorably to the HTC treatment. However, this does not consider the mass lost in the lignin extraction process. During lignin removal some hydrocarbons are removed as well, which may be equal to the additional mass lost from the untreated wood. Hemicelluloses decompose at temperatures of 180 °C [16,25] which suggests that the lignin removal process could have produced similar reactions to low temperature HTC prior to this study's experimental work. Depending on the way lignin is removed (i.e., in a thermal or chemical process), the total mass yield considering conversion from untreated feedstock to treated wood hydrochar may have a smaller mass yield value than the untreated wood hydrochar. This is because the amount of mass lost in the thermal pretreatment process in this study is unknown, and thus further analysis of the combined process energy yield is required.

3.2. Proximate Analysis

The proximate analysis on a dry basis and energy value of the raw feedstock and the product hydrochars are shown in Table 2 along with their standard deviations. The fixed carbon composition was calculated by difference, and therefore its uncertainty is dependent on the uncertainties involved in the ash and volatile matter analyses. Because the experiments were performed in duplicate—and at most in triplicates—there is great variation among the standard deviations. However, these values give a representation of the proximity of the experimental values to the mean values in similar tests. The proximate composition of the treated wood given in Table 2 is nearly identical to the untreated wood, with the largest difference reaching only 0.2 percentage points in the volatile matter, within the range that this difference may be caused by uncertainty in the measurements.

Table 2. Dry basis proximate composition and energy value of hydrochar from treated and untreated wood samples. VM—Volatile Matter; AC—Ash Content; FC—Fixed Carbon; HHV—Higher Heating Value.

Sample	**Proximate Composition ± Standard Deviations** [1]	**-**	**HTC Temperature**		
		Raw	**200 °C**	**220 °C**	**240 °C**
Untreated	VM [%]	85.7 ± 1.2	73.4 ± 0.9	64.4 ± 0.6	52.2 ± 0.6
	AC [%]	0.3 ± 0.07	0.2 ± 0.01	0.1 ± 0.10	0.2 ± 0.01
	FC [%]	14.0 ± 1.2	26.5 ± 0.9	35.5 ± 0.6	47.6 ± 0.6
	HHV [MJ/kg]	20.77 ± 0.15	22.96 ± 0.08	24.38 ±0.26	27.28 ± 0.08
Treated	VM [%]	85.9 ± 0.2	75.1 ± 0.8	68.6 ± 0.3	51.1 ± 1.0
	AC [%]	0.2 ± 0.05	0.2 ± 0.03	0.1 ± 0.05	0.4 ± 0.06
	FC [%]	13.9 ± 0.2	24.7 ± 0.8	31.3 ± 0.3	48.5 ± 1.0
	HHV [MJ/kg]	21.60 ± 0.03	23.41 ± 0.02	25.23 ± 0.02	28.27 ± 0.17

[1]—calculated based on error propagation from duplicate moisture analysis and mass loss results.

In the experiments with both untreated and treated wood, as reaction temperature is increased, the fixed carbon increases and volatile matter decreases. Ash content varies slightly, but as it accounts for less than 0.5% of the mass of the feedstock, this variation is negligible compared to the changes in fixed carbon and volatile matter with increasing reaction severity. During the HTC process, some share of the ash forming minerals are dissolved in the liquid phase [44], thus resulting in the decrease in hydrochar ash content at low reaction temperatures. At the same time, with the carbonization severity increase, the secondary reactions may result in a higher amount of ash remaining in the hydrochar. A similar tendency can be seen from Table 2: An initial decrease of the ash content for both treated and untreated samples (with the minimum at 220 °C) and a subsequent increase at 240 °C. However, the results of the present study are not comprehensive enough for the accurate evaluation of the trend.

While VM and FC trajectories are consistent between the HTC experiments with the untreated and treated wood, there is some variation between the two groups, with VM higher for the treated hydrochar at 200 °C and 220 °C and slightly lower at 240 °C. FC has the opposite relationship. Confidence intervals for the proximate composition values were calculated manually based on the propagation of error in the VM and FC values, which depend on the standard deviations of moisture content and mass loss measurements. The proximate composition of the treated wood hydrochar is not statistically significantly different from the untreated wood hydrochar at a confidence level of 95% for the experiments at 200 °C and 240 °C. The experiments at 220 °C have statistically significant differences in the mean value of VM and FC at $\alpha = 0.05$, assuming that the measurements of proximate composition and moisture content are normally distributed. However, the sample size was not large enough to assess the accuracy of this assumption. Regardless of statistical significance, the values are clearly similar between the feedstock types, and the trends in these values can be analyzed with respect to temperature. The linear trajectories of decreasing VM and increasing FC with increased reaction temperature are consistent with other studies and are expected due to the devolatilization of the cellulose and hemicellulose in the feedstock during the hydrothermal carbonization reactions [14,45]. The dependencies of volatile matter and fixed carbon contents from the HTC reaction temperature are presented in Figures 5 and 6, respectively. It can be seen that with temperature increase the hydrochar characteristics approach those of lignite and bituminous coal (especially in the case of the fixed carbon content).

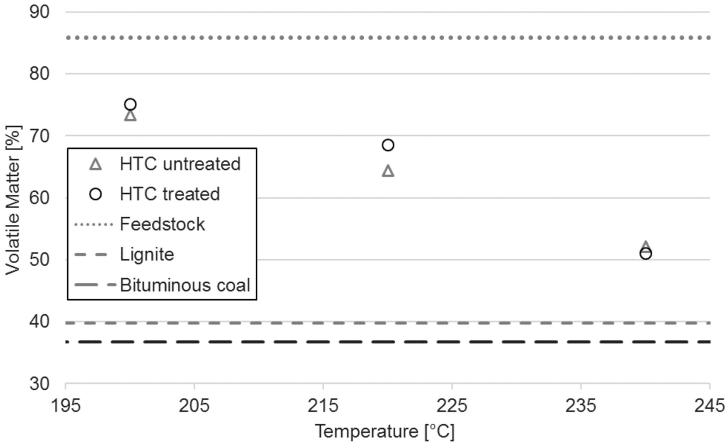

Figure 5. Volatile matter of hydrochar samples as a function of reaction temperature for untreated and treated wood.

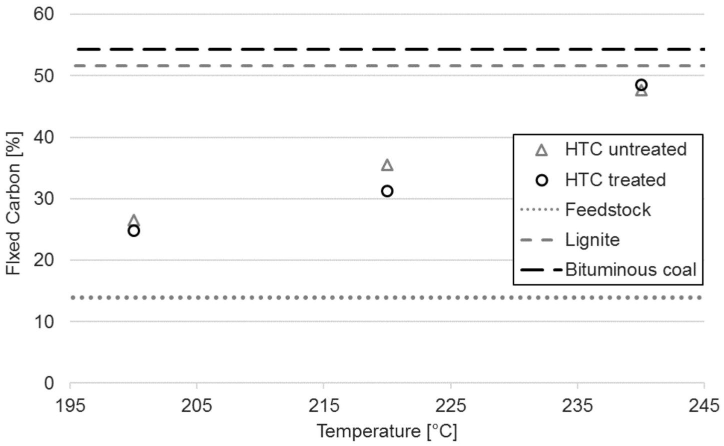

Figure 6. Fixed carbon of hydrochar samples as a function of reaction temperature for untreated and treated wood.

Ash content for the feedstock and for the produced hydrochar is substantially lower than coal, which was shown by Donahue & Rais [42] to range from 6–11% in samples of lignite, bituminous and anthracite coals. The ash contents of lignin and hemicelluloses are higher than that of cellulose [27] and therefore, with lignin values near 3% for spruce [38] the slight decrease in ash content from the untreated to treated feedstock is expected. Ash content in both the treated and untreated wood hydrochars initially decreases with reaction temperature until 220 °C, then increases after 220 °C. This matches the behavior exhibited by cellulose in HTC experiments by Kim et al. [31] and Kambo & Dutta [13].

3.3. Lignocellulosic Composition

The lignocellulosic composition of the samples on a dry ash free basis (except for the extractives that are on dry basis) is shown in Table 3. The obtained results illustrate the reaction mechanism during both treatments—The extraction pretreatment and the HTC process. As a result of the hemicelluloses and lignin extraction (180 °C for 120 min), the initial feedstock loses about 30% of holocellulose (most probably easily hydrolysable hemicelluloses). While lignin is removed in this process as well, the hemicelluloses were extracted in higher quantities, which leads to an increase in the fractional composition of lignin of all types. At the same time, the extractives amount increases notably. A similar trend was reported for aqueous soluble compounds in the case of HTC treatment of loblolly pine [46]. Such behavior can be explained by the precipitation of hemicellulose and cellulose degradation products onto the pores of the solid product.

Table 3. Lignocellulosic composition of the samples in (%) before and after hydrothermal carbonization (HTC) experiments.

Sample	**Chemical Composition (%) ± Standard Deviations** [1]	**-**	**HTC Temperature**		
		Raw	**200 °C**	**220 °C**	**240 °C**
Untreated	Extractives	3.65 ± 0.15	11.16 ± 0.18	11.23 ± 0.15	11.35 ± 0.08
	Insoluble lignin [2]	30.10 ± 2.20	50.66 ± 2.41	67.21 ± 4.99	87.85 ± 6.96
	Soluble lignin [2]	0.032 ± 0.003	0.027 ± 0.002	0.030 ± 0.002	0.039 ± 0.003
	Total lignin [2]	30.13 ± 2.20	50.69 ± 2.41	67.24 ± 4.99	87.89 ± 6.96
	Holocellulose [2]	66.22 ± 2.21	38.15 ± 2.41	21.53 ± 5.00	0.76 ± 6.96
Treated	Extractives	12.11 ± 0.20	10.22 ± 0.33	12.58 ± 0.07	11.50 ± 0.12
	Insoluble lignin [2]	37.44 ± 0.92	50.77 ± 2.51	63.90 ± 0.06	87.34 ± 2.00
	Soluble lignin [2]	0.066 ± 0.001	0.052 ± 0.002	0.016 ± 0.002	0.032 ± 0.001
	Total lignin [2]	37.50 ± 0.92	50.82 ± 2.51	63.92 ± 0.06	87.37 ± 2.00
	Holocellulose [2]	50.39 ± 0.92	38.97 ± 2.53	23.50 ± 0.10	1.13 ± 2.01

[1]—calculated from duplicate results; [2]—dry ash free basis.

A similar tendency for the extractives can be seen for the HTC process: The HTC treatment results in a certain increase of the extractives content, which is not, however, changing further with a temperature increase. As for the general distribution of the lignocellulosic components in the hydrochar samples, the values for both untreated and treated wood are quite similar. The solids obtained after HTC treatment at 240 °C were primarily comprised of insoluble lignin (about 88%) and extractives (about 11.5%). A similar tendency was reported in the work by Mäkelä et al. [47]: the aromatic character of the HTC char is increasing with HTC reaction temperature and corresponding decomposition of cellulose and hemicelluloses. The obtained results for the treated and untreated samples show that the effect of extraction on the characteristics of hydrochars is negligible. Only a small difference in the content of lignocellulosic components can be noticed between the feedstock options.

4. Conclusions

The current work shows that the spruce which has undergone extraction treatment produces chemically comparable hydrochar to the untreated spruce with a higher energy yield on average. The spruce which had previously undergone extraction had an average energy yield of 81.5% across the three reaction temperatures, 200 °C, 220 °C and 240 °C, while the raw spruce had only an average of 71.8% energy yield. The energy yield did not show a strong correlation with the temperature of the reaction. The main reason for the difference in average energy yields between the feedstocks was the difference between the mass yields between the hydrochars of the two feedstocks, as well as the improvement in HHV for the treated wood and its hydrochar products. The experiments with the spruce after extraction had higher mass yield than the experiments with the raw spruce, with the largest difference measured for the average mass yield at 200 °C of 11.3 percentage points. Energy density, quantified by HHV, increased with increasing reaction temperature for both feedstocks, ranging from 22.96 for untreated wood at 200 °C to a maximum higher heating value of 28.27 MJ/kg for treated wood hydrochar at 240 °C. The treated wood feedstock, as well as the treated wood hydrochars had higher energy density than their untreated counterparts.

The final proximate composition and energy densification factor of the hydrochars does not appear to be substantially impacted by the extraction process, with comparable values for both the treated and untreated wood hydrochars at all temperature levels. Energy densification factors were found to be correlated strongly with temperature, and the difference in the regression coefficient was not found to be statistically significantly different between the two feedstock groups, suggesting their behaviors follow the same energetic trends during upgrading.

The results of the chemical composition of the studied solids before and after HTC also proved that the extraction does not have a significant effect on the derived hydrochars. The distribution of the lignocellulosic components in case of spruce before and after extraction was quite similar: the amount of holocellulose notably decreases, while lignin content increases with an increase in HTC temperature.

The treated wood, composed of residual solid spruce after pressurized hot water extraction showed promise as a feedstock for energy upgrading, with favorable outcomes in the hydrothermal upgrading process due to losing less mass and retaining more of its original energy than raw untreated spruce wood. Further work is needed, however, to quantify the overall energy yield of the two processes combined and analyze the redundancy in chemical reactions between the lignin removal and HTC processes. Opportunities for combining or co-locating these treatment processes would also improve the economics of the system. The overall energy efficiency of the process should be considered when integrating this process into a larger bio-refinery model.

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