

Article

Hydrothermal Carbonization of Peat Moss and Herbaceous Biomass (*Miscanthus*): A Potential Route for Bioenergy

Poritosh Roy ^{1,*}, Animesh Dutta ^{1,*} and Jim Gallant ²

¹ School of Engineering, University of Guelph, Guelph, ON N1G 2W1, Canada

² REMASCO, 3811 Middle Side Road, Amherstburg, ON N9V 2Y9, Canada; jimgallant@remasco.ca

* Correspondence: poritosh@uoguelph.ca (P.R.); adutta@uoguelph.ca (A.D.); Tel.: +1-519-824-4120 (A.D.)

Received: 26 September 2018; Accepted: 15 October 2018; Published: 17 October 2018



Abstract: Peat moss and miscanthus were hydrothermally carbonized (HTC) either individually or co-processed in a different ratio to produce hydrochar. The hydrochar and pelletized hydrochar were then characterized to determine if hydrochar can be used as an alternative to coal to produce bioenergy from existing coal-fired power plants in Ontario that have already been shut down. The properties of carbonized biomass (either hydrochar or pellets) reveal that fuel grade hydrochar can be produced from peat moss or from the blend of peat moss and miscanthus (agricultural biomass/energy crops). Hydrochar either produced from peat moss or from the blend of peat moss and miscanthus was observed to be hydrophobic and porous compared to raw peat moss or raw miscanthus. The combustion indices of carbonized biomass confirmed that it can be combusted or co-combusted to produce bioenergy and can avoid slagging, fouling, and agglomeration problems of the bioenergy industry. The results of this study revealed that HTC is a promising option for producing solid biofuel from undervalued biomass, especially from high moisture biomass. Co-processing of peat moss with rural biomass, a relatively novel idea which can be a potential solution to heat and power for the rural communities/agri-industry that are not connected with national grids and alleviate their waste management problems. In addition, the hydrochar can also be used to run some of the existing coal-fired power plants that have already been shut down in Ontario without interrupting investment and employment.

Keywords: hydrothermal carbonization (HTC); peat moss; miscanthus; co-processing; physicochemical properties; bioenergy

1. Introduction

Peat moss has been used as a source of energy in boreal and temperate regions [1]. Presently, most of the harvested peat moss is used for non-fuel application in Canada, especially in horticulture as a soil supplement [2,3]. Sphagnum (peat moss) biomass can be grown on degraded peatland and can be an alternative to fossil peat for horticultural application as well as to reduce greenhouse gas (GHG) emission [2]. Biomass handling and transportation are the major constraints in a large scale bioenergy industry [4], which can be minimized if biomass is carbonized, such as hydrothermally carbonized (HTC) and densified [5,6]. It has also been reported that the strength and combustion characteristics of HTC biomass are better compared with raw and torrefied biomass [7].

Generally, peat moss decomposes over time and releases nutrients (nitrogen, phosphorus, and potassium); however, it can become a carbon source when decomposition is lower than the above- and belowground accumulation [8]. The accumulation and decomposition rate of peat moss depends on the communities of peat moss [9]. In a natural peatland, biomass accumulation exceeds the

decomposition rate of organic matter and becomes a carbon reservoir [10,11], which could be a potential source of bioenergy to replace depleting fossil fuels such as coal or fossil peat. Canada is recognized as a leader of peat moss industries in the world for her sustainable practices where 65% of peat moss is certified [12]. Although peat moss accumulation surpasses the harvesting, peat moss decomposition results in greenhouse gas (GHG) emission, either from horticultural or other applications or on natural peatlands. Canada has about 113.6 million ha of peatland, which is scattered in different provinces and only about 17,000 ha is used for peat moss harvesting [3,13]. In Ontario, 29.4% area is covered by peatland [14]. Although 70 million tons of peat moss are accumulated each year in Canada [3], only 1.3 million tons are harvested [15,16]. On the other hand, peatlands in Canada sequestered about 23 million tons of carbon per year [17]. It is also reported that many existing and new peatland sites can be revegetated with *Sphagnum* for peat moss harvesting [3].

The decomposition rate of peat moss depends on the carbon-nitrogen ratio, temperature, and availability of water and the state of peat moss [8,18,19]. For example, the decomposition rate of untreated biomass (raw biomass) is greater than that of treated biomass (i.e., biochar) [20,21]. In the case of horticultural application, the decomposition rate is noted to be greater than the natural peatland, and peat moss decomposition and its end use contributed 71% GHG to the life cycle of peat moss [22]. Yearly the decomposition or loss rate (k) of peat moss varies from 0.05–0.20 [23,24].

In addition, Ontario has phased out coal and shut down all the coal-fired power plants to combat rising GHG emissions, which contributed to rising electricity prices [25,26]. Therefore, an alternative renewable fuel is desired to keep the present coal-fired power plants in operation as well as abate GHG emissions. Peat moss, rich in carbon content could be an alternative to coal if properly treated. Hydrothermal carbonization (HTC) is a promising technology to convert wet biomass into fuel grade solid biofuel without the expensive drying treatment and can handle a wide range of lignocellulosic biomass providing favorable energy balance compared to alternate processes [5,27,28]. Hydrothermally treated biomass, i.e., hydrochar, has a wide application such as a soil amendment to abate GHG emission, energy, and removal of contaminants [29] or to absorb nutrient from a nutrient-rich environment [30]. In addition, the process water rich in potassium can be used for crop irrigation to recover some of the nutrients [5]. Consequently, peat moss was treated with or without agricultural biomass (an energy crop, i.e., miscanthus; i.e., co-processed) to produce hydrochar and then they were pelletized to produce densified biofuels (pellets). The hydrochar and pelletized hydrochar have been characterized to determine whether hydrochar can be used as an alternative to coal to run the power plants that have already been shut down.

2. Materials and Methods

Peat moss (*Sphagnum*) and miscanthus (an energy crop) were collected from the local market and farm, respectively. The samples were stored in the laboratory in air-tight bags and were used to produce hydrochar and pellets.

2.1. Carbonization

Peat moss available in the local market is high in moisture content (MC; about 50%), thus peat moss with (T4-T5; i.e., blend of peat moss and miscanthus) or without (T1-T3, i.e., only peat moss) herbaceous biomass as well as only herbaceous biomass (T7) was hydrothermally carbonized (HTC) by using a Parr reactor (600 mL bench top reactor, Moline, IL, USA). Biomass treated at 230–260 °C which is suitable for briquetting/pelletization [7,31]. A proportional-integral-derivative (PID) temperature controller has been used to control the carbonization temperature to 240 °C for 15, 30, and 45 min. Feedstock (40 g bone dry matter) and water (200–250 g water depending on the initial moisture content of feedstocks) was poured in the reactor vessel and stirred for about 3 min to ensure the complete wetting. After the wetting period, 10 min of standby time was allowed when miscanthus was blended with peat moss in the carbonization process to ensure the wetting of biomass. It was also ensured that the feedstock was submerged in water in the reactor. The reactor was sparged with N₂ gas to make an

inert condition, and then the reactor was pressurized with N₂ gas to 1.38 MPa (200 psi) before heating the reactor. Once the temperature rose to the desired carbonization temperature, the carbonization time started accounting. However, the pressure was not controlled and the reactor pressure varied from 1.38–4.83 MPa (200–700 psi) during the experimental periods. After completing the desired carbonization time, the reactor vessel was immediately cooled (5–7 min) to room temperature with the help of cold water. Then the release valve of the reactor was loosened to release the gaseous products. The liquid was separated by using a filter paper (20 µm) and collected for further analysis. The solid portion was dried overnight in a muffle furnace at 105 °C and stored in a zipper bag for further experiments (characterization, pelletization, hydrophobicity).

2.2. Proximate Analysis

The proximate analysis was conducted by using the ASTM standards (Moisture: ASTM-E871; Ash: ASTM-E1755; Volatile matter: ASTM-E872). Each feedstock was placed in the furnace (Thermo Scientific-F48055-60, Waltham, MA, USA) and was dried at 105 °C for 16 h. The dried samples were placed in the furnace at 575 °C for 5 h to determine ash content. The volatile matter was measured by burning the samples at 950 °C for 7 min.

2.3. Ultimate Analysis

The biomass samples were analyzed with a CHNS-O analyzer (Flash 200 CHNS-O, Organic Elemental Analyzer, Thermo Fisher Scientific, and The Netherlands) based on ASTM D5373-08. The samples were dried at 105 °C for 24 h prior to the ultimate analysis. Then the samples were combusted at 925 °C in a Helium atmosphere, while the reduction was carried out at 650 °C.

2.4. Heating Value

The oven dried sample was used to determine the higher heating value (HHV) of the feedstock. The HHV was measured with a bomb calorimeter (IKA-C200, Wilmington, NC, USA). Pure oxygen was used to pressurize the vessel to 3 MPa (30 bar) before being ignited with a cotton thread, and the calorific value of the sample was recorded.

2.5. Mass and Energy Yield

The following equations were used to determine the mass and energy yield, and the energy densification ratio of the carbonized biomass.

$$\text{Mass yield, \%} = \frac{\text{Mass of preated biomass}}{\text{Mass of raw biomass}} \times 100 \quad (1)$$

$$\text{Energy, \%} = \text{Mass yield, \%} \times \text{Energy densification ratio} \quad (2)$$

$$\text{Energy densification ratio} = \frac{\text{HHV of preated biomass}}{\text{HHV of raw biomass}} \quad (3)$$

2.6. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

The samples were mounted on the surface of a standard aluminum SEM stub with a carbon tape. A Cressington 108 Auto sputter coater was used to coat the samples with a 10 nm gold film to provide the conductivity. The images of samples were collected with a scanning electron microscope (FEI Inspect S50, Japan) at an accelerating voltage of 20 kV with an aperture of 3.5 by an ETD secondary electron detector. The ash samples were mounted on carbon tapes (without gold coating) on the sample holders and the images were collected (four spectrums and the average are reported) with an Oxford X-Max20 Silicon Drift Detector using AZtecEnergy EDX microanalysis software.

2.7. Combustion Indices of Hydrochar

Slagging, fouling, and the agglomeration potential of feedstock were determined based on the alkali index (Equation (4)), base to the acid ratio (Equation (5)), and bed agglomeration index (Equation (6)). The alkali index (*AI*) is calculated from the ratio of the mass of the alkali oxides (K_2O and Na_2O) in ash that produced from the feedstock and the energy content (*GJ*) in each unit of feedstock [32,33]. *BAI* relates to the agglomeration of fluidized bed reactors [34].

$$\text{Alkali index, } AI = \frac{kg(K_2O + Na_2O)}{GJ} \quad (4)$$

$$\text{Base and acid ratio, } R = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \quad (5)$$

$$\text{Bed agglomeration index, } BAI = \frac{\%(Fe_2O_3)}{\%(K_2O + Na_2O)} \quad (6)$$

2.8. Pelletization

The modified Parr single-pellet press (Model #2912) has been used to produce pellets from untreated and treated feedstocks [35,36]. The modified pelletizer consists of the load cell, piston, cylindrical die, brand heater, die holder, and PID controller. Samples were exposed to room conditions to bring them to their equilibrium moisture content before being used in the pelletization process [36]. The temperature of the die was controlled at 100 °C. The sample was placed on the die and 8.6 MPa (1250 psig) pressure was applied and hold for 30 s [36]. Then the pellet was collected and stored in an air-tight plastic bag for further analysis.

2.9. Equilibrium Moisture Content (EMC)

The moisture content of the sample that is in thermodynamic equilibrium with the moisture of the surrounding atmosphere at a given relative humidity, temperature, and pressure is known as the equilibrium moisture content (EMC) of that sample. The raw and carbonized samples were exposed to a controlled environment (humidity 75% and temperature 25 °C) for 24 h [36]. The samples were then dried in an oven at 105 °C for 24 h (16 h) and the moisture content of the samples was determined (Equation (1)).

$$MC = \frac{M_i - M_d}{M_d} \quad (7)$$

where,

MC = Moisture content of the sample

M_i = Initial mass of the sample

M_d = Mass of the oven dried sample

2.10. Hardness of Pellets

The hardness of pellets was measured with an Instron Machine (Model #5965) using a cylindrical probe. The probe diameter and load cell were 5 mm and 5 kN, respectively. The test speed was controlled to 0.1 mm/s [37,38] and compressed to an extension of 2.5 mm. The pellet was horizontally placed at the center of the horizontal plate as well as the center of the probe to measure the peak force (Figure 1) of a single pellet, which is considered to be the hardness of the pellet.

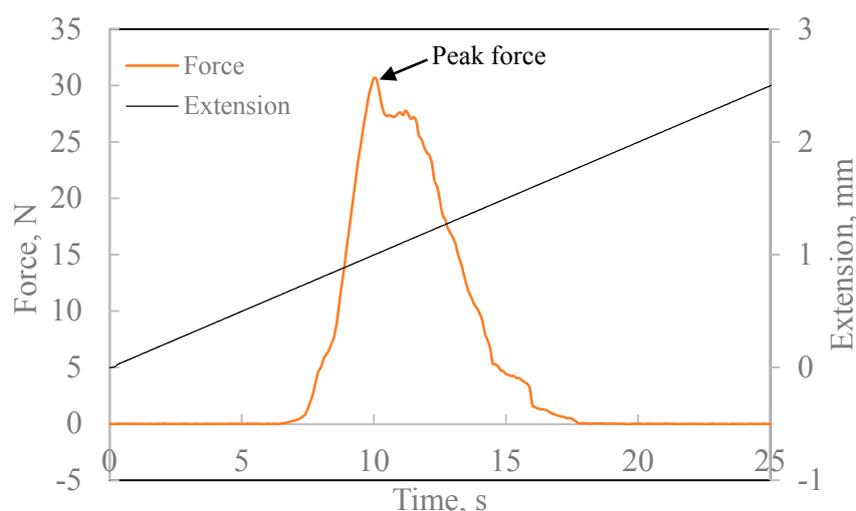


Figure 1. Force deformation curve and extension.

2.11. Durability

Pellets were dropped on a metal plate to measure the durability of untreated and treated biomass pellets. Each pellet was dropped for 4 times from a height of 1.85 m [36,39]. After dropping, the mass of the pellet was measured. The percentage of mass retained with pellets (with the largest part) after dropping is defined as the durability of pellets.

3. Results and Discussion

3.1. Effect of Processing Conditions on the Compositions of Hydrochar

Usually, peat moss contains high moisture, consequently it has a low energy density (14 MJ/kg) that cannot be used as a fuel or co-combusted in coal-fired power plants. In addition, biomass contains a higher amount of volatile matter, thus, not only does it have poor combustion efficiency and harmful gas emissions, it cannot be combusted with other fuels because of the difference in energy and bulk density [40]. The moisture, volatile matter (VM) and ash content in the collected peat moss were 47.3%, 66.0%, and 6.6%, respectively. On the other hand, miscanthus contained 4.4% moisture, 87.5% VM, and 0.8% ash [36] and the energy density was 18.6 MJ/kg. The components of it in feedstock also varied depending on the types of feedstock (Table 1). However, VM, ash and fixed carbon (FC) in treated peat moss varied from 52–60%, 6–7% and 33–40%, respectively (Table 1), depending on the treatment conditions. In the case of treated miscanthus, VM, ash, and FC were 74.5%, 0.9%, and 24.6%, respectively. The proximate analysis of untreated and treated biomass shows that VM reduced in the treated biomass, while FC increased and no significant change was observed in ash content. In contrast, a reduction of ash content in the hydrochar was reported where the hydrochar was produced from miscanthus/corn stalk/sawdust [7,36], which might be because of the differences in treatment temperature and type of biomass, which need be confirmed by further study.

Physicochemical properties of treated biomass confirmed that HTC improves the quality of the biomass, which can be used as fuel or maybe co-combusted in the existing coal-fired power plants. The ultimate analysis revealed that carbon content is higher in treated biomass; however, nitrogen and sulfur content was reduced with HTC (Table 2), thus improves the quality of biomass. It seems that the treatment time has a mild impact on the fuel quality. Pretreated biomass has higher energy density and combustion characteristics compared with untreated biomass [36,41]. HTC improves the quality of peat moss (i.e., carbonized peat moss can be used in the existing coal-fired power plants) because fuel properties of hydrochar produced from peat moss are found to be similar to those of lignite (Table 2). This study also reveals that peat moss can be carbonized with energy crops (miscanthus) or with other biomass to produce fuel grade hydrochar even blended with 75% miscanthus.

Table 1. Major components in the feedstocks.

Feedstock	Composition, %			Reference
	Hemicellulose	Cellulose	Lignin	
Peat moss	24.1	17.1 (44.2 *)	18.0 (25–40 ^)	[42–44]
Miscanthus	36.3	38.6	11.5	[18]

Note: The values in the parenthesis accompanied with symbols (^ and *) are taken from the following references, *: 44 and ^: 43.

Table 2. Physicochemical properties of untreated and treated feedstock.

Sample	Proximate Analysis (%)				Ultimate Analysis (%)			
	VM	Ash	FC	N	C	H	S	O
T ₀	65.96	6.56	27.47	1.17	51.09	5.46	0.23	42.05
T ₁	52.44	7.08	40.48	1.32	59.55	4.80	0.21	34.12
T ₂	51.43	6.18	42.39	1.40	61.55	5.07	0.21	31.78
T ₃	51.55	6.67	41.78	1.40	62.13	4.98	0.19	31.30
T ₄	60.27	5.38	34.35	1.03	60.32	5.07	0.15	33.43
T ₅	61.74	5.67	32.59	0.72	55.66	4.67	0.10	38.85
T ₆	63.89	2.22	33.90	0.61	66.60	5.29	0.07	27.43
T ₇	74.58	0.87	24.55	0.29	68.67	5.12	0.00	25.92
UMS	87.50	1.57	10.93	0.21	46.66	6.00	0	45.34

Note: HTC was conducted at 240 °C. T₀: Untreated peat moss; T₁, T₂, and T₃: Peat moss treated for 15, 30, and 45 min, respectively; T₄–T₇: treated for 15 min; T₄: 75% peat moss & 25% miscanthus; T₅: 50% peat moss & 50% miscanthus; T₆: 25% peat moss & 75% miscanthus; T₇: Miscanthus; VM: Volatile matter; FC: Fixed carbon; UMS: Untreated miscanthus.

3.2. Effect of Processing on the Mass Yield, Energy Yield, and HHV

The mass yield of treated peat moss was 70–74%, depending on the treatment time. On the other hand, mass yield was found to be 48–70%, depending on the amount of miscanthus was blended with peat moss. The higher the miscanthus in the feedstock the lower the mass yield, because untreated miscanthus contains a greater amount of VM and part of which was lost during HTC; however, the energy density increased. Although the energy density increased with a greater amount of miscanthus in the blended feedstock, energy yield was found to be slightly lower because of lower mass yield (Table 3). The calculated energy yield was 68–89%, depending on the treatment time and the ratio of peat moss and miscanthus. The maximum mass and energy yield was observed in the case of T₁ (when peat moss was treated for 15 min). Therefore, it seems that HTC of peat moss for only 15 min would be the best option to produce fuel grade hydrochar to replace coal, which might enable the production of power from some of the existing coal-fired power plants by using renewable resources without any interruption in investment and employment.

Table 3. Effect of processing conditions on the higher heating value (HHV), mass and energy yield.

Feedstock	HHV, MJ/kg	EDR	Mass Yield, %	Energy Yield, %
T ₀	21.29 *	1.00	100	100
T ₁	25.21	1.20	73.75	88.69
T ₂	25.37	1.21	72.60	87.86
T ₃	25.79	1.23	70.34	86.54
T ₄	25.16	1.23	70.06	86.51
T ₅	25.07	1.27	62.95	79.74
T ₆	27.80	1.45	47.74	69.07
T ₇	27.80	1.49	45.87	68.45

Note: HTC was conducted at 240 °C. T₀: Untreated peat moss; T₁, T₂, and T₃: Peat moss was treated for 15, 30 and 45 min, respectively; T₄–T₇: treated for 15 min; T₄: 75% peat moss & 25% miscanthus; T₅: 50% peat moss & 50% miscanthus; T₆: 25% peat moss & 75% miscanthus; T₇: Miscanthus; * Energy content in peat moss 14 MJ/kg (as received); HHV: Higher heating value; EDR: Energy density ratio.

3.3. Effect of Hydrothermal Carbonization on the Equilibrium Moisture Content (EMC)

The equilibrium moisture content (EMC) of untreated samples varied from 14.6–15.6%. On the other hand, the EMC varied from 5.1–9.5% in the case of treated biomass. The higher EMC was observed in the case of untreated samples compared with treated samples (T₁–T₇), because of the reduction of the moisture absorption capacity of the hydrochar [45]. The EMC of the samples decreased because of the carbonization treatment, which reduces volatile matter and decomposes hemicellulose and lignin, thus improving the hydrophobicity of the treated samples [36,46,47].

3.4. Hardness and Durability of Pellets

The HTC process alters the physicochemical properties of biomass, thus it eases the grinding process compared with untreated biomass. In addition, the densification process improves mass and energy density of feedstock [48], easing the handling and transportation of feedstock such as pellets. Figure 2 represents the pellets produced from treated and untreated samples. The hardness of pellets decreased because of the HTC treatment and depends on the treatment time. It seems that the longer the treatment time the lower the hardness of pellets, and pellets produced from the untreated sample had greater hardness compared with the treated sample (Table 4). This table also shows that the collapsing time and extension reduced in the case of pellets produced from treated biomass compared with untreated one. The decomposition of hemicellulose and lignin reduces the binders and solid bonds between the carbonized particles, and thus there are more pore spaces that promote relative movements of particles, which result in lower strength [46]. The EMC of the sample might play an important role in the hardness of the pellets [49,50] as it works as a lubricant and binder during the pelletization process [51]. It has also been reported that the strength is dependent on the moisture content, species of biomass, and the pelletizing pressure [37]. The hardness of pellets produced from untreated peat moss was observed to be greater than that of the carbonized samples either only from treated peat moss or from the blend of peat moss and miscanthus.

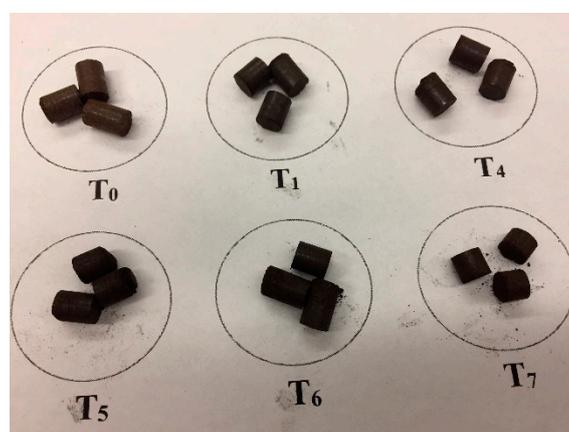


Figure 2. Pellets from untreated and carbonized feedstock.

Table 4. Hardness and durability of pellets.

Samples	Time, s	Extension, mm	Hardness, N	Durability, %
T ₀	11.1	1.1	53.9	89.9
T ₁	10.6	1.1	46.7	80.0
T ₂	10.3	1.0	29.3	60.4
T ₃	9.8	1.0	22.7	62.9
T ₄	10.6	1.1	40.9	72.3
T ₅	9.8	1.0	12.9	66.2
T ₆	9.6	1.0	21.0	60.9
T ₇	7.7	0.8	7.5	59.6

The optimum moisture content of co-pelletization is reported to be 10–15% [51]. Untreated samples have higher EMC thus may have influenced the hardness of pellets except the pellets produced from carbonized miscanthus, which is consistent with other studies [36]. In addition, the co-carbonization and subsequent pelletization might affect the hardness of the pellets [46]; however, the hardness tends to be influenced by the ratio of the samples that were co-pelletized. The pellets from co-pelletized samples had a lower hardness [51] compared with peat moss only. The pellets produced from the co-carbonized samples have greater hardness compared with pellets that are produced from miscanthus only, but not the pellets from the peat moss. The decomposition of hemicellulose and depolymerization of cellulose along with the softening of lignin [52] caused by the HTC process improves the friability [36,47]. The strength of the pellets also decreased with the severity of carbonization (200–350 °C) [53]; beyond this temperature, the strength increased [54,55]. In contrast, the durability of engineered pellets noted to be increased with the increasing fraction of hydrocarbon [56].

Carbonized biomass contains a lower amount of chemically bonded water and compounds that have a low melting point that acted as a binding agent during pelletization at around 100 °C, thus it affects the strength of pellets from carbonized samples [57]. The lignin in the biomass softens when heated and enhances the binding characteristics of materials during pelletization [58]; however, natural lignin does not have an effect if the HTC temperature is controlled to less than 260 °C [59]. It is also noted that the natural binders create solid bridges between particles during the pelletization, thus increasing the hardness [60] and the durability of the pellets. The durability of pellets produced from untreated samples was greater than the pellets from carbonized samples [56], consequently, pellets from untreated peat moss have higher durability (Table 4). In addition, the durability of pellets seems to be dependent on the treatment times and the ratio of peat moss and miscanthus. The durability of pellets decreased with the increase of miscanthus in the feedstock.

The SEM images confirmed that the HTC process has a significant impact on the structure of biomass. HTC reduces the hemicellulose and cellulose contents in hydrochar compared with the untreated biomass [31]. The reduction of hemicellulose and cellulose results in the porous structure of hydrochar. The untreated biomass has a well-defined structure (Figure 3: 0, MS) which has been changed to be a porous structured biomass; i.e., hydrochar (Figure 3: T₁, T₄–T₆). It is worthy to mention that a porous structure was observed in hydrochar even with 75% miscanthus was blended in the feedstock (the blends contain 25%, 50%, and 75% miscanthus in T₄, T₅, T₆, respectively). Consequently, the porous structure of hydrochar samples can improve the contaminant adsorption capacity, thus it can be a potential source for wastewater treatment [61,62] and broaden the scope of hydrochar for commercial application.

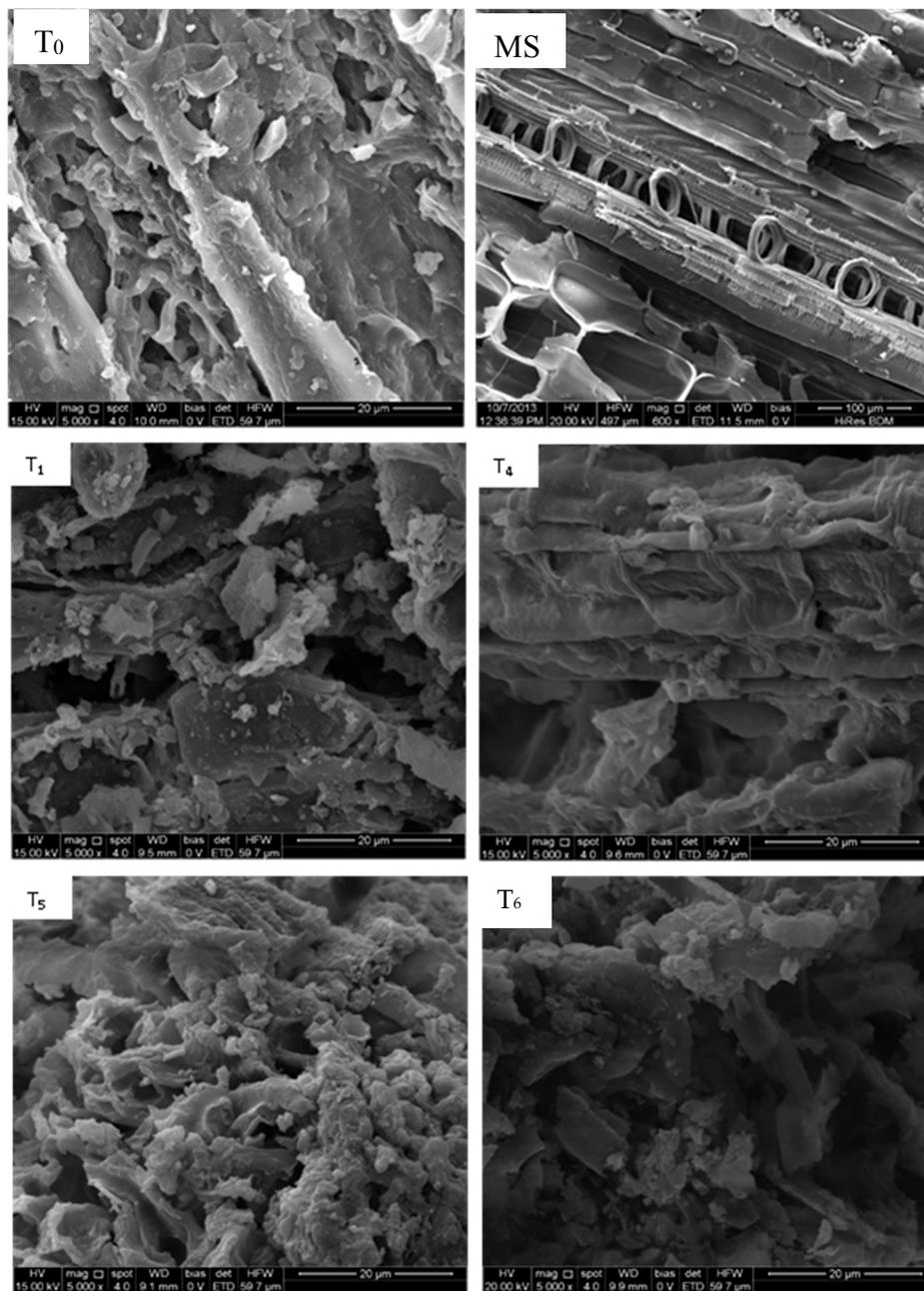


Figure 3. Scanning electron microscope (SEM) of untreated and carbonized samples (T_0 : untreated peat moss; MS: untreated miscanthus T_1 : carbonized peat moss; T_4 – T_6 : Carbonized peat moss and miscanthus blend).

3.5. Effect of HTC on the Combustion Indices of Hydrochar

Most of the lignocellulosic biomass is rich in inorganic components (Ca: calcium, Mg: magnesium, P: phosphorous, K: potassium, Na: sodium, S: sulfur, and Fe: iron), especially agricultural biomass (Table 5). Usually, these elements are left, and from their oxides that occur during combustion they are responsible for fouling, slagging and agglomeration, and are also corrosive [63]. It seems that the HTC process enables the production of a hydrochar that has a porous structure [64], which might have prompted the leaching of some of the alkali and alkaline metals [31,63], and thus produced a lesser amount of oxides (Table 5). The concentration of chemicals (oxides) decreased if treated in HTC processes; however, the oxides concentration depended on the ratio of peat moss and miscanthus. The higher the ratio of miscanthus and peat moss, the greater the oxides may be because of the presence

of a higher amount of alkali and alkaline metals in untreated miscanthus compared with peat moss. Consequently, HTC can be a promising option to improve the combustion properties of biomass which can replace coal in the energy industry.

Table 5. Effect of hydrothermal carbonization hydrothermally carbonized (HTC) on the chemical composition of ash.

Sample	SiO ₂	P ₂ O ₅	CaO	MgO	K ₂ O	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	TiO ₂
T ₀	11.00	1.18	17.60	12.93	1.35	5.23	6.40	0.00	4.23	0.00
T ₁	18.03	0.43	15.68	8.05	1.35	8.15	11.53	0.00	1.65	0.18
T ₄	23.63	1.00	11.10	5.13	2.15	9.80	9.63	0.00	1.98	0.75
T ₅	23.08	0.63	12.53	5.93	1.83	8.35	8.68	0.13	1.83	0.00
T ₆	36.50	1.97	7.03	3.07	2.30	9.07	5.03	0.00	1.83	0.00
T ₇	34.78	11.45	15.00	2.40	1.73	1.00	0.85	0.80	0.00	0.00
* MS	54.71–63.12	6.03–10.60	7.61–10.35	3.46–6.07	16.39–21.79	0.45–0.69	0.18–0.37	0.20–0.36	0.28–0.85	0.01–0.04

Note: * Untreated miscanthus [19].

The AI, base to the acid ratio ($R_{b/a}$) and BAI of hydrochar varied from 0.00001–0.00017, 0.42282–2.61941, and 0.49275–3.84167, respectively, depending on the ratio of peat moss and miscanthus. The least indices were observed in cases of biochar that was produced only from peat moss. Vamvuka & Zografos [33] noted that a fuel may or may not cause slagging or fouling if its AI varies from 0.17–0.34 kg/GJ; however, beyond this range, fouling or agglomeration occurred [65]. On the other hand, bed agglomeration takes place if BAI is lower than 0.15 [34]. This study confirmed that the fuel properties of both biomass (peat moss and miscanthus) can be improved by the HTC process and reduce the fouling, agglomeration, and slagging in the combustion process to produce heat and power from hydrochar. However, the hydrochar produced from only peat moss seems to have better combustion indices compared to either hydrochar from miscanthus or from the blend of peat moss and miscanthus (Table 6). The AI, $R_{b/a}$ and BAI of raw miscanthus were 0.145–0.359, 0.466–0.701 and 0.012–0.02, respectively, depending on fertilizer application (0–80 kg/ha) and harvesting season (Fall/Spring), which may or may not be suitable [32]. Therefore, the HTC process can be used to improve the fuel quality of high moisture biomass and replace coal or co-combusted with coal in existing coal-fired power plants without interrupting the investment and employment in heat and power industry.

Table 6. Effect of HTC on the slagging, fouling and agglomeration indices.

Sample	Alkali Index(AI)	Base to Acid ratio, ($R_{b/a}$)	Bed Agglomeration Index (BAI)
T ₀	0.00017	2.61941	1.14798
T ₁	0.00008	1.45161	3.84167
T ₄	0.00009	0.87710	2.33333
T ₅	0.00008	0.97932	2.37671
T ₆	0.00003	0.42282	1.21774
T ₇	0.00001	0.55835	0.49275

Note: T₀: Untreated peat moss; T₁, T₂, and T₃: Peat moss was treated for 15, 30 and 45 min, respectively; T₄–T₇: treated for 15 min; T₄: 75% peat moss & 25% miscanthus; T₅: 50% peat moss & 50% miscanthus; T₆: 25% peat moss & 75% miscanthus; T₇: Miscanthus.

4. Conclusions

Hydrothermal carbonization of peat moss seems to be a promising option to produce hydrocarbon because of its high moisture content (MC) and improve the fuel characteristics of biomass. This study also revealed that herbaceous biomass can be co-carbonized for producing fuel-grade hydrochar that can have properties such as lower grade coal. The energy content in carbonized biomass varied from 25–28 MJ/kg, and the energy yield varied from 68–89% depending on the treatment conditions. The slagging, fouling, and agglomeration indices also revealed that hydrochar can be combusted or co-combusted and can avoid slagging, fouling and agglomeration problems in the bioenergy

industry, because alkali and bed agglomeration indices were found to be 0.00001–0.00017 and 0.49–3.8, respectively. The hydrochar produced either from only peat moss or the blend can replace coal, and produce power from some of the existing coal-fired power plants in Ontario (which have already been shut down in an attempt to phase out coal) without interrupting investment and employment.

Author Contributions: P.R. has conducted the study. He was supervised by A.D. and J.G.

Acknowledgments: The authors are grateful to the NSERC Discovery (Grant No. 400495) and the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) (Grant No. 200474) for the financial support to this study.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Towards Climate-responsible Peatlands Management. Available online: <http://www.fao.org/3/a-i4029e.pdf> (accessed on 27 February 2018).
2. Sphagnum Farming for Replacing Peat in Horticultural Substrates. Available online: <http://www.fao.org/3/a-i4417e.pdf> (accessed on 5 February 2018).
3. Environment Canada. North American Waterfowl Management Plan. Available online: <https://www.fws.gov/birds/management/bird-management-plans/north-american-waterfowl-management-plan.php> (accessed on 27 February 2018).
4. Brown, D.; Rowe, A.; Wild, P. A techno-economic analysis of using mobile distributed pyrolysis facilities to deliver a forest residue resource. *Bioresour. Technol.* **2013**, *150*, 367–376. [[CrossRef](#)] [[PubMed](#)]
5. Hitzl, M.; Corma, A.; Pomares, F.; Renz, M. The hydrothermal carbonization (HTC) plant as a decentral biorefinery for wet biomass. *Catal. Today* **2015**, *257*, 154–159. [[CrossRef](#)]
6. Tang, Y.; Cong, W.; Xu, J.; Zhang, P.; Liu, D. Ultrasonic vibration-assisted pelleting for cellulosic biofuels manufacturing: A study on in-pellet temperatures. *Renew. Energy* **2015**, *76*, 296–302. [[CrossRef](#)]
7. Wu, S.; Zhang, S.; Wang, C.; Mu, C.; Huang, X. High-strength charcoal briquette preparation from hydrothermal pretreated biomass wastes. *Fuel Process. Technol.* **2018**, *171*, 293–300. [[CrossRef](#)]
8. Bragazza, L.; Buttler, A.; Siegenthaler, A.; Mitchell, E.A.D. Plant Litter Decomposition and Nutrient Release in Peatlands. *Carbon Cycl. North Peatl.* **2008**, *184*, 99–110.
9. Davis, R.C. Peat respiration and decomposition in Antarctic terrestrial moss communities. *Biol. J. Linn. Soc.* **1980**, *14*, 39–49. [[CrossRef](#)]
10. Frolking, S.; Talbot, J.; Jones, M.C.; Treat, C.C.; Kauffman, J.B.; Tuittila, E.-S.; Roulet, N. Peatlands in the Earth's 21st century climate system. *Environ. Rev.* **2011**, *19*, 371–396. [[CrossRef](#)]
11. Yu, Z.C.; Beilman, D.W.; Frolking, S.; MacDonald, G.M.; Roulet, N.T.; Camill, P.; Charman, D.J. Peatlands and their role in the global carbon cycle. *Eos. Trans. Am. Geophys Union* **2011**, *92*, 97–98. [[CrossRef](#)]
12. Association of Canadian Sphagnum Peat Moss. SAFA Case Study: A first Industry Social Responsibility Report for the Canadian Sphagnum Peat Moss Association using SAFA Guidelines. Available online: http://tourbehorticole.com/wp-content/uploads/2015/07/CSPMA_ISR_Report_2014_web_LW.pdf (accessed on 25 February 2018).
13. Environment Canada. National Inventory Report 1990–2011: Greenhouse Gas Sources and Sinks in Canada. Available online: http://publications.gc.ca/collections/collection_2013/ec/En81-4-2011-1-eng.pdf (accessed on 25 February 2018).
14. Rubec CDA. Canadian Wetland Inventory: Hard Issues and Realities. Available online: <http://nawcc.wetlandnetwork.ca/Can%20Peat%20Harvesting%202001-1.pdf> (accessed on 15 February 2018).
15. Moss CSP, Association. Compost Council of Canada Peat Industry Sustainability Presentation. 2013. Available online: http://www.compost.org/conf2013/FC3_Partners_in_the_field/2_Sustaining_the_Peat_Industry_CSPMA.pdf (accessed on 25 February 2018).
16. Sustainability Canadian Horticultural Peat Industry Position Paper. Available online: <http://tourbehorticole.com/wp-content/uploads/2015/09/CSPMA-Sustainability-Position-Paper.pdf> (accessed on 12 March 2018).

17. Carlson, M.; Chen, J.; Elgie, S.; Henschel, C.; Montenegro, Á.; Roulet, N.; Scott, N.; Tarnocai, C.; Wells, J. Maintaining the role of Canada's forests and peatlands in climate regulation. *For. Chron.* **2010**, *86*, 434–443. [CrossRef]
18. Belyea, L.R. Separating the effects of litter quality and microenvironment on decomposition rates in a patterned Peatland. *OIKOS* **1996**, *77*, 529–539. [CrossRef]
19. Mathur, S.P.; Levesque, M.P. Relationship between acid phosphatase activities and decomposition rates of twenty-two virgin peat materials. *Commun. Soil Sci. Plant Anal.* **1980**, *11*, 155–162. [CrossRef]
20. Ok, Y.S.; Uchimiya, S.M.; Chang, S.X.; Bolan, N. *Biochar: Production, Characterization, and Applications*; CRC Press: Boca Raton, FL, USA, 2015.
21. Rudz, P. Carbon and Nutrient Dynamics of Downed Woody Debris in a Northern Hardwood Forest. Master's Thesis, University of Toronto, Toronto, ON, Canada, 2013.
22. Cleary, J.; Roulet, N.T.; Moore, T.R. Greenhouse Gas emissions from canadian peat extraction, 1990–2000: A life-cycle analysis. *AMBIO J. Hum. Environ.* **2005**, *34*, 456–461. [CrossRef]
23. Frohling, S.; Roulet, N.T.; Moore, T.R.; Richard, P.J.H.; Lavoie, M.; Muller, S.D. Modeling northern peatland decomposition and peat accumulation. *Ecosystems* **2001**, *4*, 479–498. [CrossRef]
24. Moore, T.R. Growth and net production of Sphagnum at five fen sites, subarctic eastern Canada. *Can. J. Bot.* **1989**, *67*, 1203–1207. [CrossRef]
25. Authority OP. Achieving Balance: Ontario's Long-term Energy Plan. Available online: <http://www.ontariopetroleuminstitute.com/wp-content/uploads/2014/06/Achieving-Balance-Ontarios-Long-Term-Energy-Plan.pdf> (accessed on 5 March 2018).
26. Canada CE. Ontario's Coal Phaseout in Perspective. Available online: <http://cleanenergycanada.org/ontarios-coal-phaseout-perspective/> (accessed on 5 March 2018).
27. Kambo, H.S.; Dutta, A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sustain. Energy Rev.* **2015**, *45*, 359–378. [CrossRef]
28. Hoekman, S.K.; Broch, A.; Felix, L.; Farthing, W. Hydrothermal carbonization (HTC) of loblolly pine using a continuous, reactive twin-screw extruder. *Energy Convers. Manag.* **2017**, *134*, 247–259. [CrossRef]
29. Fang, J.; Zhan, L.; Sik, Y.; Gao, B. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. *J. Ind. Eng. Chem.* **2018**, *57*, 15–21. [CrossRef]
30. Takaya, C.A.; Fletcher, L.A.; Singh, S.; Anyikude, K.U.; Ross, A.B. Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes. *Chemosphere* **2016**, *145*, 518–527. [CrossRef] [PubMed]
31. Kambo, H.S.; Dutta, A. Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel. *Energy Convers. Manag.* **2015**, *105*, 746–755. [CrossRef]
32. Kludze, H.; Deen, B.; Dutta, A. Impact of agronomic treatments on fuel characteristics of herbaceous biomass for combustion. *Fuel Process. Technol.* **2013**, *109*, 96–102. [CrossRef]
33. Vamvuka, D.; Zografos, D. Predicting the behaviour of ash from agricultural wastes during combustion. *Fuel* **2004**, *83*, 2051–2057. [CrossRef]
34. Skrifvars, B.J.; Backman, R.; Hupa, M.; Sfiris, G.; Abyhammar, T.; Lyngfelt, A. Ash behaviour in a CFB boiler during combustion of coal; peat or wood. *Fuel* **1998**, *77*, 65–70. [CrossRef]
35. Narayanasamy, L.; Murugesan, T. Degradation of Alizarin Yellow R using UV/H₂O₂ advanced oxidation process. *Environ. Sci. Technol.* **2014**, *33*, 482–489.
36. Kambo, H.S.; Dutta, A. Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. *Appl. Energy* **2014**, *135*, 182–191. [CrossRef]
37. Stelte, W.; Holm, J.K.; Sanadi, A.R.; Barsberg, S.; Ahrenfeldt, J.; Henriksen, U.B. Fuel pellets from biomass: The importance of the pelletizing pressure and its dependency on the processing conditions. *Fuel* **2011**, *90*, 3285–3290. [CrossRef]
38. Roy, P.; Shimizu, N.; Kimura, T. Effect of temperature distribution on the quality of parboiled rice produced by traditional parboiling process. *Food Sci. Technol. Res.* **2007**, *10*, 254–260. [CrossRef]
39. Kaliyan, N.; Morey, R.V. Factors affecting strength and durability of densified biomass products. *Biomass Bioenergy.* **2009**, *33*, 337–359. [CrossRef]
40. Khan, A.A.; de Jong, W.; Jansens, P.J.; Spliethoff, H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Process. Technol.* **2009**, *90*, 21–50. [CrossRef]

41. Roy, P.; Dutta, A.; Acharya, B.; Deen, B. An investigation of raw and torrefied lignocellulosic biomasses with CaO during combustion. *J. Energy Inst.* **2018**, *91*, 584–594. [[CrossRef](#)]
42. FAO (Food and Agriculture Organization of the United Nations). The Main Characteristics of Tropical Peats-FAO (Food and Agriculture Organization of the United Nations). Available online: <http://www.fao.org/docrep/x5872e/x5872e06.htm> (accessed on 5 February 2018).
43. Farmer, V.C.; Morrison, R.I. Lignin in sphagnum and phragmites and in peats derived from these plants. *Geochim. Cosmochim. Acta* **1964**, *28*, 1537–1546. [[CrossRef](#)]
44. Plank, N. The nature of cellulose in sphagnum. *Am. J. Bot.* **1946**, *33*, 335–337. [[CrossRef](#)]
45. Sermyagina, E.; Saari, J.; Kaikko, J.; Vakkilainen, E. Hydrothermal carbonization of coniferous biomass: Effect of process parameters on mass and energy yields. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 551–556. [[CrossRef](#)]
46. Cao, L.; Yuan, X.Z.; Li, H.; Li, C.Z.; Xiao, Z.H.; Jiang, L.B.; Hunag, B.H.; Xiao, Z.H.; Chen, X.H.; Wang, H.; et al. Complementary effects of torrefaction and co-pelletization: Energy consumption and characteristics of pellets. *Bioresour. Technol.* **2015**, *185*, 254–262. [[CrossRef](#)] [[PubMed](#)]
47. Puig-Arnavat, M.; Ahrenfeldt, J.; Henriksen, U.B. Validation of a Multiparameter Model to Investigate Torrefied Biomass Pelletization Behavior. *Energy Fuels* **2017**, *31*, 1644–1649. [[CrossRef](#)]
48. Yan, W.; Acharjee, T.C.; Coronella, C.J.; Vasquez, V.R. Thermal pretreatment of lignocellulosic biomass. *Environ. Prog. Sustain. Energy* **2009**, *28*, 435–440. [[CrossRef](#)]
49. Ahn, B.J.; Chang, H.-S.; Lee, S.M.; Choi, D.H.; Cho, S.T.; Han, G.-S.; Yang, I. Effect of binders on the durability of wood pellets fabricated from *Larix kaemferi* C. and *Liriodendron tulipifera* L. sawdust. *Renew. Energy* **2014**, *62*, 18–23. [[CrossRef](#)]
50. Carone, M.T.; Pantaleo, A.; Pellerano, A. Influence of process parameters and biomass characteristics on the durability of pellets from the pruning residues of *Olea europaea* L.. *Biomass Bioenergy* **2011**, *35*, 402–410. [[CrossRef](#)]
51. Jiang, L.B.; Liang, J.; Yuan, X.Z.; Li, H.; Li, C.Z.; Xiao, Z.H.; Huang, H.Z.; Wang, H.; Zeng, G.M. Co-pelletization of sewage sludge and biomass: The density and hardness of pellet. *Bioresour. Technol.* **2014**, *166*, 435–443. [[CrossRef](#)] [[PubMed](#)]
52. Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels Bioprod. Biorefin.* **2010**, *4*, 160–177. [[CrossRef](#)]
53. Larsson, S.H.; Rudolfsson, M.; Nordwaeger, M.; Olofsson, I.; Samuelsson, R. Effects of moisture content; torrefaction temperature; and die temperature in pilot scale pelletizing of torrefied Norway spruce. *Appl. Energy* **2013**, *102*, 827–832. [[CrossRef](#)]
54. Hu, Q.; Yang, H.P.; Yao, D.D.; Zhu, D.C.; Wang, X.H.; Shao, J.G.; Chen, H.P. The densification of bio-char: Effect of pyrolysis temperature on the qualities of pellets. *Bioresour. Technol.* **2016**, *200*, 521–752. [[CrossRef](#)] [[PubMed](#)]
55. Ding, L.; Yoshikawa, K.; Fukuhara, M.; Xin, D.; Muhan, L. Development of an ultra-small biomass gasification and power generation system: Part 1. A novel carbonization process and optimization of pelletization of carbonized wood char. *Fuel* **2017**, *210*, 674–683. [[CrossRef](#)]
56. Reza, M.T.; Uddin, M.H.; Lynam, J.G.; Coronella, C.J. Engineered pellets from dry torrefied and HTC biochar blends. *Biomass Bioenergy* **2014**, *63*, 229–238. [[CrossRef](#)]
57. Li, H.; Liu, X.H.; Legros, R.; Bi, X.T.T.; Jim Lim, C.; Sokhansanj, S. Pelletization of torrefied sawdust and properties of torrefied pellets. *Appl. Energy* **2012**, *93*, 680–685. [[CrossRef](#)]
58. Van Dam, J.E.; van den Oever, M.J.; Teunissen, W.; Keijsers, E.R.; Peralta, A.G. Process for production of high density/high performance binderless boards from whole coconut husk: Part 1: Lignin as intrinsic thermosetting binder resin. *Ind. Crops Prod.* **2004**, *19*, 207–216. [[CrossRef](#)]
59. Reza, M.T.; Lynam, J.G.; Vasquez, V.R.; Coronella, C.J. Pelletization of biochar from hydrothermally carbonized wood. *Environ. Prog. Sustain. Energy* **2012**, *31*, 225–234. [[CrossRef](#)]
60. Kaliyan, N.; Morey, R.V. Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass. *Bioresour. Technol.* **2010**, *101*, 1082–1090. [[CrossRef](#)] [[PubMed](#)]
61. Regmi, P.; Garcia Moscoso, J.L.; Kumar, S.; Cao, X.; Mao, J.; Schafran, G. Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process. *J. Environ. Manag.* **2012**, *109*, 61–69. [[CrossRef](#)] [[PubMed](#)]
62. Titirici, M.M.; White, R.J.; Falco, C.; Sevilla, M. Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. *Energy Environ. Sci.* **2012**, *5*, 6796–6822. [[CrossRef](#)]

63. Reza, M.T.; Lynam, J.G.; Uddin, M.H.; Coronella, C.J. Hydrothermal carbonization: Fate of inorganics. *Biomass Bioenergy* **2013**, *49*, 86–94. [[CrossRef](#)]
64. Funke, A.; Ziegler, F. Perspective: Jatropha cultivation in southern India: Assessing farmers' experiences. *Biofuels Bioprod. Biorefin.* **2012**, *6*, 246–256.
65. Dayton, D.C.; Jenkins, B.M.; Turn, S.Q.; Bakker, R.R.; Williams, R.B.; Belle-Oudry, D.; Hill, L.M. Release of inorganic constituents from leached biomass during thermal conversion. *Energy Fuel.* **1999**, *13*, 860–870. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).