Journal of Sustainable Bioenergy Systems, 2017, 7, 138-148
http://www.scirp.org/journal/jsbs
ISSN Online: 2165-4018
ISSN Print: 2165-400X

Hydrothermal Carbonization of Deciduous Biomass (*Alnus incana*) and Pelletization Prospects

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How to cite this paper: Kc, R., Babu, I., Alatalo, S., Föhr, J., Ranta, T. and Tiihonen, I. (2017) Hydrothermal Carbonization of Deciduous Biomass (*Alnus incana*) and Pelletization Prospects. *Journal of Sustainable Bioenergy Systems*, **7**, 138-148.
https://doi.org/10.4236/jsbs.2017.73010

Received: August 3, 2017
Accepted: September 10, 2017
Published: September 13, 2017

Abstract

Thermal treatment of biomass has been attracting attention for a decade or so, especially torrefaction. However, for the past few years, wet pyrolysis, also known as hydrothermal carbonization (HTC), has been getting some attention. Hydrothermal carbonization is a thermal treatment of biomass in the presence of water in a temperature range of 180˚C - 260˚C. This method of treating biomass has some benefits which others do not, such as it can handle extremely wet biomass. However, treating biomass may not be enough for practical use. It may need to be transported and stored. Thus, this study explored the idea of pelletizing the HTC biomass. The mechanical strength of the HTC pellets was found to be 93%, whereas, higher heating value (HHV) (dry basis) was found to be 4% higher than the corresponding white pellets. The initial results with some limited parameters indicated that it would be possible to pelletize without binder. However, extensive research on energy balance and economic assessment would be necessary to achieve economic feasibility.

Keywords

Sustainable, Bioenergy, Hydrothermal Carbonization, Hydrochar, Pelletization

1. Introduction

Biomass has been recognized and promoted as a potential opportunity to reduce carbon emissions from the energy sector. The complicated biomass properties such as lack of uniformity, high moisture content and low mass density, hinder its wider applicability. However, pre-treatment and/or modification such as dry and wet torrefaction of biomass are promising solutions to the aforementioned difficulties [1].

Hydrothermal carbonization (HTC), also known as wet pyrolysis, is a thermochemical treatment of biomass based materials taking place in the presence of water at moderate temperature ranging from 180˚C to 260˚C [1] [2] [3]. HTC may be more suitable for raw materials with varying moisture percentage because reaction takes place in a wet environment and eliminates the pre-drying phase which could potentially eliminate the energy intensive phase [4]. As the HTC involves a pressurized reaction environment in saturated water, it is significantly different than traditional dry torrefaction where biomass is pre-dried and then torrefied in the dry and oxygen deficient environment. However, the final product, hydrochar, is found to be homogeneous compared to raw material and similar to torrefied biomass [1] [5]. According to the study by [6], −OH groups in biomass are partly removed by dehydration reaction during wet pyrolysis, which reduces its capacity to absorb water, thus, making the final product more hydrophobic than the raw material is. Furthermore, the combustion behavior of hydrochar is somewhat similar to lignite meaning they are suitable for co-combustion [5] [6]. The viability of co-combustion with coal in large power plants suggests a significant increase in its demand and subsequently a potential to reduce fossil fuel consumption.

The bulk density of the biomass is one of the crucial factors in long distance transportation because of the constraint payload and fuel consumption related to it. Biomass pellets are the most traded biomass commodity due to their higher energy density compared to the loose biomass (e.g. wood chips and saw dust) [7]. In addition to economic benefits, diminished freight transportation means less greenhouse gas (GHG) emissions. The bulk energy density of wood saw dust (moisture ~50%) is about 540 kWh/m^3 whereas the bulk energy density of traditional white pellets is about 2.8 MWh/m^3 [8]. Furthermore, the bulk energy density of torrefied biomass pellets could be achieved up to 5.7 MWh/t [9]. The significant increase in bulk energy density indicates that the transportation related cost could be halved with torrefaction.

The purpose of this study was to analyze HTC biomass of grey alder (Alnusincana) and the prospect of densification by means of pelletization. Grey alder also known as thin-leafed alder is a deciduous tree. The wood chips of grey alder are common for smoking fish and meat in cooking. The elemental analysis, functional groups analysis using Fourier Transform Infrared Spectroscopy (FTIR) and magnified pictures of components using Scanning Electronic Microscope (SEM) are analyzed for the potential differences due to varying residence time. In the case of pellets, properties such as mechanical strength and calorific values were analyzed. The grey alder was chosen as a raw material because very little has been reported about it in biomass upgrading, especially HTC.

Lignin is a natural polymer found in wood which acts as a glue [10]. It is one of the crucial components in wood that helps as a binder in pelletization. Since the primary aim of this study was to study the possibility of pelletization of HTC hardwood (Alder) biomass, the aim is also to determine whether an additional binder is necessary for the pelletization.

2. Materials and Methods

The packages of grey alder chips were bought from the supermarket for the experiments because of uniform size and moisture of chips. The moisture content of raw chips was 10.3%. The chemical composition of grey alder is lignin (24.8%), cellulose (38.3%), glucuronoxylan (25.8%), glucomannan (2.8%) other polysaccharides (2.3%), residuals (1.4%) and extractives (4.6%) [11]. The biomass was purchased from the Finnish supermarket packaged in a polyethylene bags. The size distribution of chips is illustrated in **Table 1**.

2.1. Hydrothermal Carbonization (HTC)

HTC of Alder was performed in a 230 ml reactor shown in **Figure 1**. The batch reactor is made up of stainless steel with a PTFE inner vessel. For the reaction, biomass was mixed with ionized water in 1:4 w/w ratio and enclosed in the reactor. The mixture contained 30 g of biomass and 120 ml of ionized water. The

Table 1. Size distribution of raw chips.

Size class [mm]	Share %	Cumulative %
<2.000	1.20%	1.20%
2.000 - 3.150	1.10%	2.30%
3.150 - 8.000	74.30%	76.60%
8.000 - 16.000	23.40%	100%
>16.000	0.00%	100%

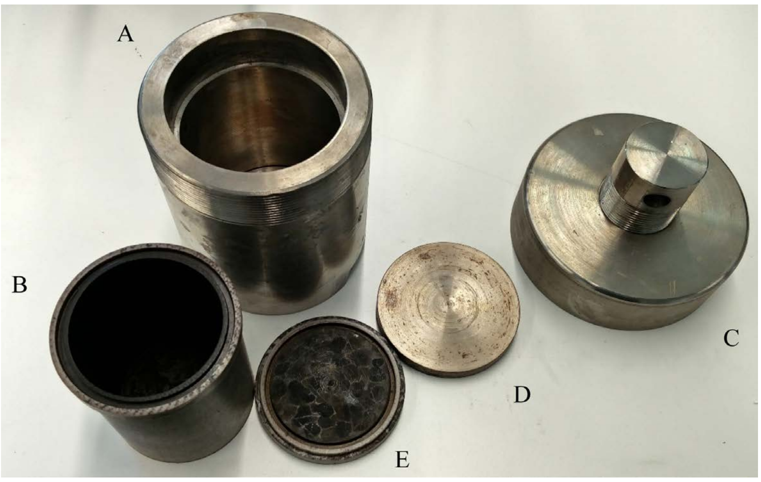

Figure 1. The components of laboratory scale HTC reactor. (A): outer chamber, (B): reactor, (C): outer cap, (D): mid-cover, (E): inner cap).

oven was preheated to 220˚C and placed in the oven for three different reaction times (90 minutes, 120 minutes and 240 minutes). As the reactor was heated, the pressure inside the reactor rises up to 4.6 MPa, according to Reza *et al.* (2012). However, the pressure was not measured during this experiment. After the carbonization, the biomass was filtered and collected in an air-sealed plastic bag.

2.2. Pelletization

The hydrochar 220˚C for 90 minutes was pelletized in the pelletizer (AmandusKahl) as shown in **Figure 2**. The carbonized biomass, which is kept in sealed plastic bags after the pyrolysis was dried at 70˚C for 8 hours. The dry carbonized biomass is then pelletized in a laboratory scale pelletizing machine shown in **Figure 3** with an 8 mm matrix with 34 mm length. For the sake of comparison, raw alder chips are also pelletized but in a smaller matrix due to the stiffness of the chips in a small-power pelletization machine. The stiffness in the matrix caused the matrix to be overheated which causes an unnecessary effect on the final result. The raw alder chips and HTC biomass and pellets are presented in **Figure 3** and **Figure 4**, respectively. The schematic process is shown in **Figure 5**.

Figure 2. Laboratory scale pelletization machine manufactured by Amandus Kahl.

Figure 3. Carbonized biomass pellets with 8 mm diameter and 34 mm depth matrix. The circled pellets are visibly excessively roasted in the matrix.

Figure 4. Raw alder chips (left) and carbonized alder chips (right).

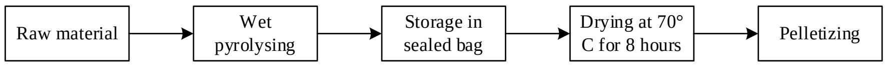

Figure 5. Schematic diagram of an entire process of HTC implemented.

3. Results

3.1. Proximate and Ultimate Analysis

The appearance of the HTC biomasses is distinctive; as the reaction time increased the color of the product which seems to be darker. Also, the texture of the product appears to be softer as the reaction time increased. The proximate and ultimate *i.e.* elemental composition, fixed carbon and ash content of white pellets and HTC pellets have been performed according to the accredited methods. From the analysis, it can be seen that volatile matter has decreased by about 4.8% in HTC pellets compared to white pellets, whereas the amount of fixed carbon is increased by 4.6%. The detailed similarities and differences, as well as respective accredited methods, are shown in Table 2.

3.2. Mechanical and Energetic Analysis

The physical and calorific analysis of white and HTC pellets are presented in Table 3. The mechanical strength, moisture content and bulk density were determined following the accredited methods, however, the amount of the pellets were less than is required in the standards. The moisture content of the white pellet is significantly low (1.9%) because raw alder chips had a moisture content of only 10.3%, unlike the industrial chips used for energy production purposes. Their usual moisture content can be as high as 50% (weight). According to Li *et al*. (2012), an ideal moisture content of the wood pellets should be between 7% and 9% [12] because lower moisture content may result in significantly lower mechanical strength. In this study, the mechanical strength of white pellets was found to be 64.4%. On the other hand, the mechanical durability of HTC pellets is found to be 93.1% which is less than reported by Reza *et al*. (2012) in their research. However, the durability of HTC pellets is comparable to torrefied pellets reported by Ranta *et al*. (2016).

The bulk density of HTC pellets is found to be 685 kg/i-m^3, which is 12% higher than the corresponding white pellets. Similarly, HHV of the HTC pellets is found to be 20.85 MJ/kg on a dry basis, which is 4% higher than the corresponding white pellets. In contrast, LHV of the HTC pellets (as received) is 19.55

Table 2. Proximate and ultimate analysis of white pellets and HTC pellets.

Analysis	White Pellets	HTC pellets	Standards
	Ultimate analysis (dry, wt%)		
C	49.3	51.9	EN ISO 16948, EN 15104, EN 15407, ISO 29541
H	6	6	EN ISO 16948, EN 15104, EN 15407, ISO 29541
N	0.22	0.33	EN ISO 16948, EN 15104, EN 15407, ISO 29541
S	0.02	0.02	ASTM D 4239 (mod), EN ISO 16994, EN 15289
O (calculated)	43.8	40.8	EN ISO 16993
	Proximate analysis (dry, wt%)		
Volatile	84.8	80	EN ISO 18123, EN 15148, EN 15402, ISO 562
Fixed Carbon (calculated)	14.5	19.1	
Ash	0.7	0.9	EN ISO 18122, EN 14775, EN 15403

Table 3. Proximate and ultimate analysis of white pellets and HTC pellets.

Analysis	White Pellets	HTC pellets	Standards
Moisture content (%)	1.9	8.5	EN 14774-2, CEN/TS 15414-2, ISO 589
Bulk density (kg/i-m^3)	611	685	EN ISO 17828
Mechanical Durability (%)	64.4	93.1	EN ISO 17831-1
Gross calorific value (HHV) (MJ/kg, d)	20.04	20.85	EN 14918, EN 15400, ISO 1928
Net calorificd value (LHV) (MJ/kg, d)	18.73	19.55	EN 14918, EN 15400, ISO 1928
Net calorificd value (LHV) (MJ/kg, ar)	18.33	17.68	EN 14918, EN 15400, ISO 1928
Bulk energy density (MWh/i-m^3, ar)	3.11	3.36	

MJ/kg, which is about 3% lower than the corresponding white pellets. The possible reason could be the significantly low moisture content in white pellets than the HTC pellets.

3.3. FT-IR

In order to understand type structural features and especially surface functional groups, FTIR studies were performed. IR spectra of HTC treated hydrochars (*i.e.* HTC 90, HTC 120 and HTC 240), and raw biomass was studied using FT-IR (Bruker vertex 70). In this study, a reaction temperature of 220˚C is kept constant while reaction time varies from 90 minutes to 240 minutes The FT-IR spectra analysis is shown in Figure 6.

Lignocellulosic materials are rather heterogeneous in which IR peaks are reached from lignin, cellulose, and hemicellulose. The IR spectra of hydrothermally treated wood chips are presented in Figure 6. The IR spectra of all HTC treated materials have similarities, however, increased temperature indicated changes in the distribution of functional groups of the materials in which aromatic functionalities are more pronounced. All samples show a broad band at 3300 cm^{-1} referring to the hydroxyl groups (–OH) and aliphatic structures at wavelength 2919 - 2829 cm^{-1} which is attributed to the –CH stretching of in aromatic methoxy groups and in methyl groups from side chains [13]. Bands at 1700 - 1730 cm^{-1} refer to the carbonyl/carboxyl groups which appear more pronounced in the sample HTC 240 (*i.e.* 1702 cm^{-1}) Bands at ~1600, ~1500 and ~1450 cm^{-1} refer to the aromatic skeletal carbon structure. These peaks are more

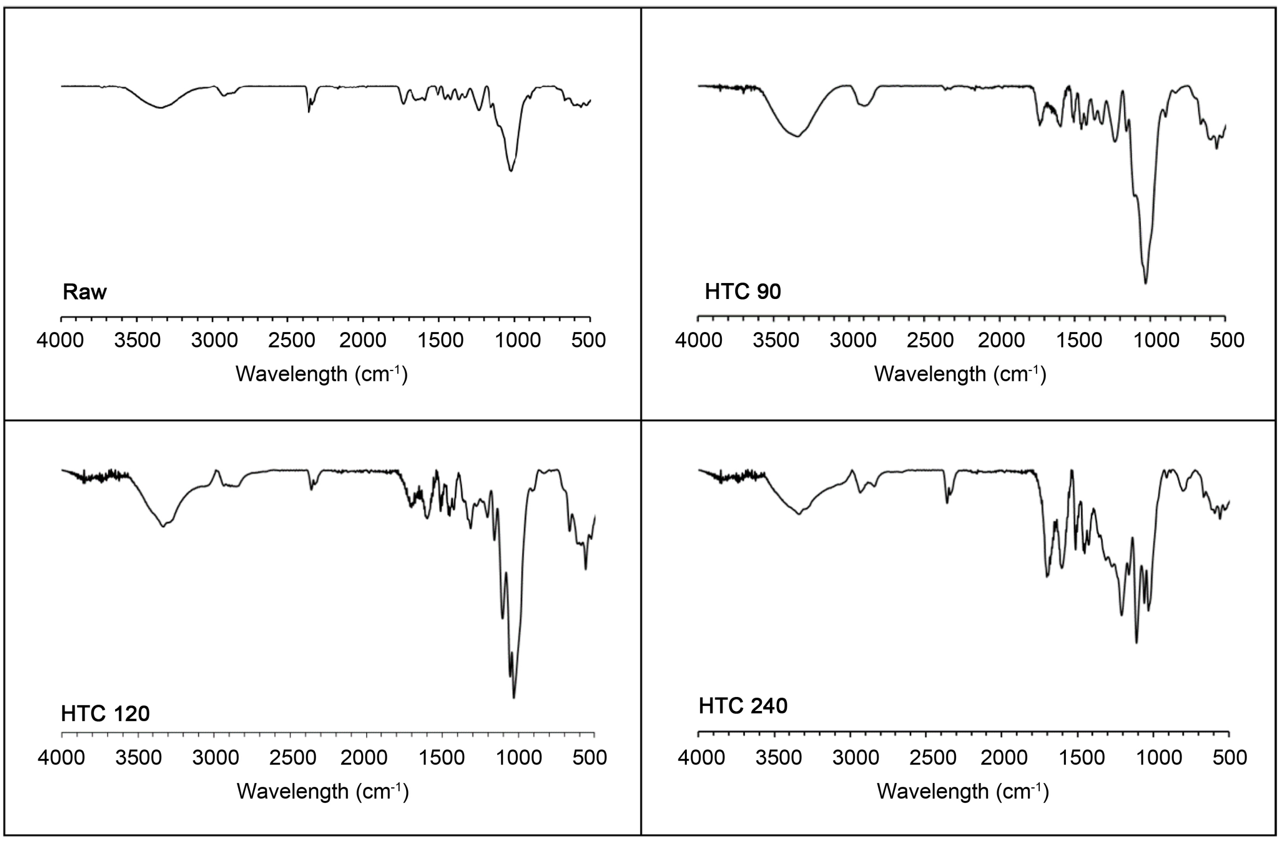

Figure 6. FT-IR spectra of raw material (Raw) and different hydrochars (*i.e.* HTC 90, HTC 120 and HTC 240). Reaction time during the HTC remained constant (220˚C) but reaction time was altered.

pronounced in HTC 240 (*i.e.* 1596 cm^{-1}, 1512 cm^{-1} and 1452 cm^{-1}) than HTC 120 or HTC 90. This may be related to the reaction time during HTC which eases the fragmentation of the lignocellulosic structure and further on the formation of aromatic end products typical to HTC [14]. Bands at wavelength 950 - 1225 cm^{-1} refer to the aromatic C-H in plane band.

3.4. Scanning Electron Microscope (SEM) Picture Analysis

SEM studies allowed us to evaluate morphological changes of HTC treated hydrochars. Images of raw biomass, HTC biomass treated at 220˚C for 90 minutes (HTC90), 120 minutes (HTC120) and 240 minutes (HTC240) are shown in **Figure 7**. All pictures shown in **Figure 7** are 600 times magnified. A regular pattern is visible in the raw biomass in picture A which is then distorted in picture B, HTC biomass (220˚C, 90 minutes). However, as the reaction time becomes longer such as in picture C, which has a reaction time of 120 minutes, the further integration of components is observable. Furthermore, picture D, which

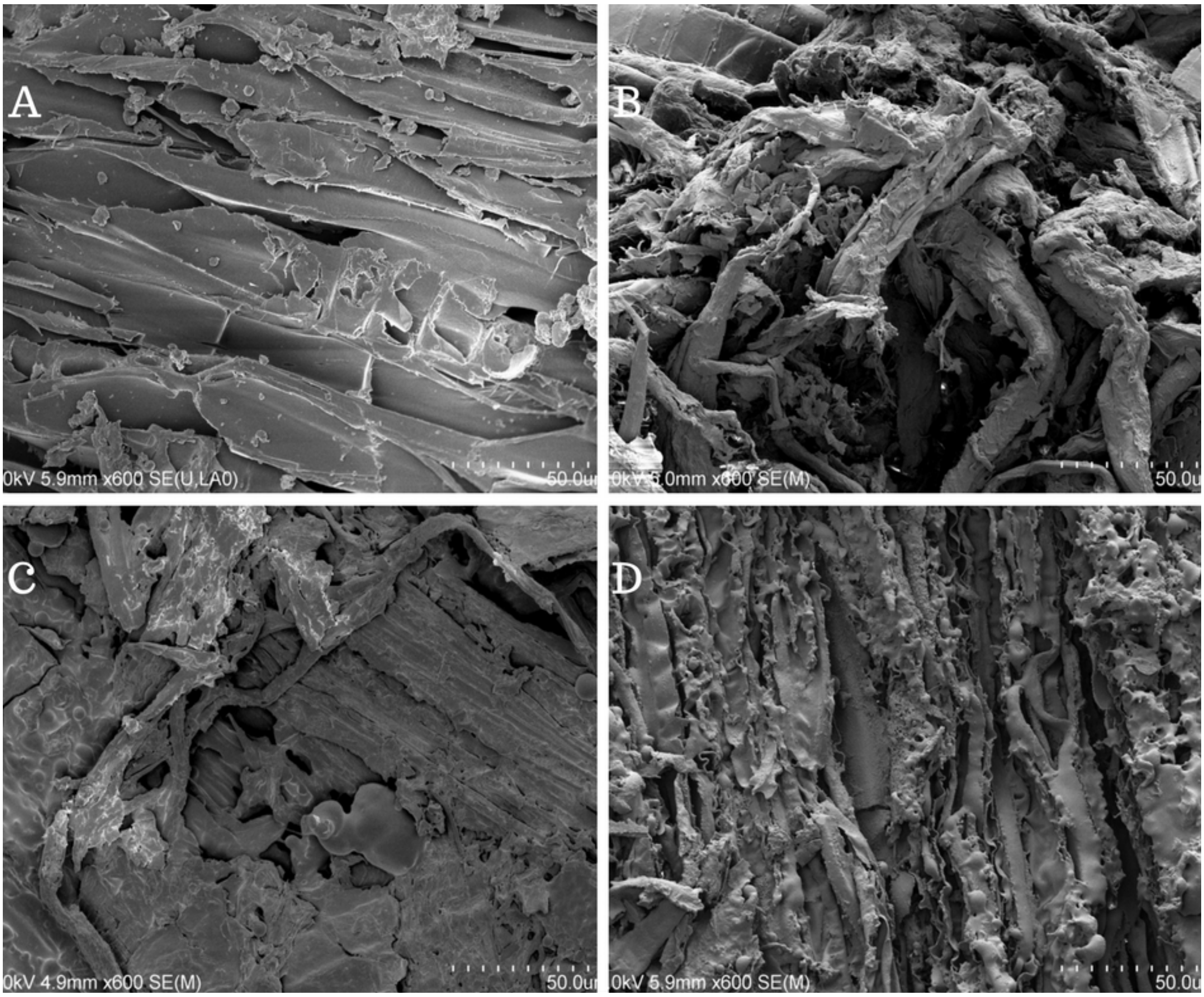

Figure 7. SEM images (magnification 600×) of raw wood (A), HTC90 (B), HTC120 (C), HTC240 (D) samples.

is an HTC biomass (220˚C, 240 minutes) shows indication of melting particles.

4. Discussion

4.1. Physical and Mechanical Properties

The visible appearance of the pellets looks compact, roasted and very similar to torrefied pellets as reported by Ranta *et al*. (2016). However, some of the pellets are more roasted than others, shown as circled in **Figure 3**. The possible reason could be overheating of the matrix of the laboratory scale pelletizer (5 kW). This may potentially have affected negatively on the LHV of the HTC pellets. A similar impact may have occurred on the mechanical durability of HTC pellets which is also comparatively lower than the torrefied pellets reported by Ranta *et al*. (2016).

4.2. Thermal Properties

The effect of moisture content in both types of the pellet is visible as the LHV (as received) of the HTC pellet is lower than the corresponding white pellets. However, the bulk energy density of HTC pellets is 8% higher than that of white pellets, meaning carbonization has increased the energy value of biomass which is an encouraging and positive of the study.

The HHV of the HTC pellets is somewhat comparable to the results reported by [3] where 200˚C reaction temperature resulted in HHV of 21.6 MJ/kg. However, in the same study, 260˚C reaction temperature has resulted in HHV 26.4 MJ/kg, which is significantly higher than the findings of this study. Similarly, [6] has reported incremental HHV of various biomass according to the increasing reaction temperature. However, none of the studies represented used Alder as a biomass. Nonetheless, this development suggests that the reaction temperature applied in this study may be too low for the optimum results. On the other hand, it would be wise to remember that the ultimate parameters for the commercialization of energy product such as pellets are energy input, energy output and production cost which are not within the scope of this study. Thus, a comprehensive study that includes the aforementioned aspects would be able to illustrate further about the viability of HTC pellets on a commercial scale.

4.3. Comparison of HTC Pellets with Torrefied Pellets

The SEM image (600 times magnified) of torrefied pellets (B) from the study by Ranta *et al*. (2016) and HTC pellets (A) from this study are compared and shown in **Figure 8**. The HTC_PEL has visible similarities with torrefied pellets (TOR_PEL). The lignin in pelletized biomass (**Figure 8**) shows binding unlike the undisturbed fibers in non-pelletized HTC biomass (**Figure 7**). This indicates that compression and temperature generated due to the pelletizing sieve may have had an effect on binding the pellets.

5. Conclusions

From the experiments, it can be concluded that the pelletization of HTC biomass

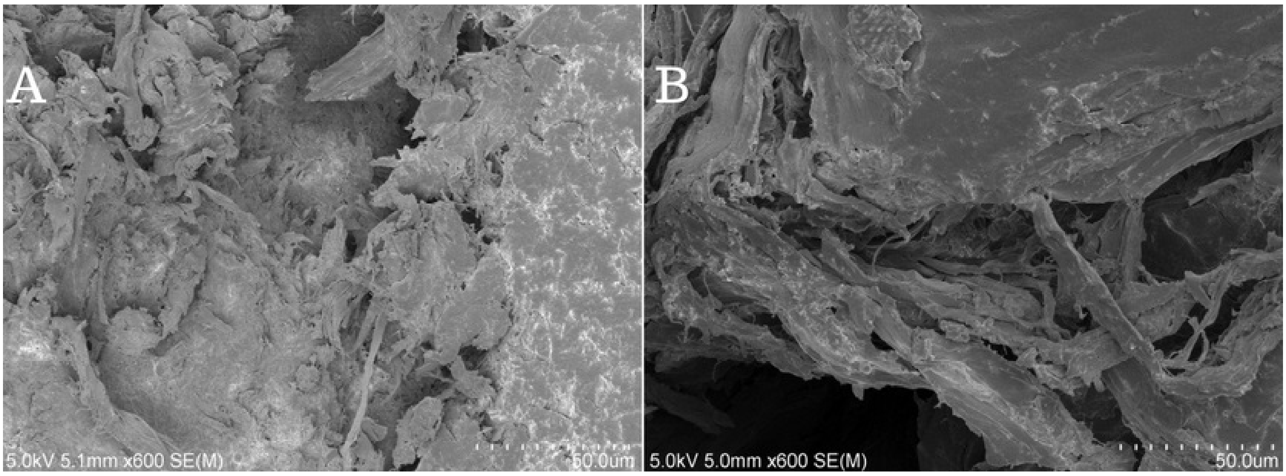

Figure 8. 600 times magnified SEM pictures of HTC_PEL (A) and TOR_PEL(B).

is possible and potentially beneficial compared to its wood chips counterpart. Undestroyed particles in pelletized HTC biomass with intact bridges as compared to torrefied pellet shown in **Figure 7** indicate that additional binder may not be necessary for the pelletization of HTC biomass with parameters of 90 minutes run time and 220˚C reaction temperature.

However, further research would be necessary to identify optimum parameters such as temperature and reaction time for the efficient energy yield. Furthermore, chemical pretreatment before carbonization should also be assessed for potential benefits. Identifying the behavior of lignin in different reaction times is a major challenge. The solution to these challenges could be to isolate the lignin from the material and experiment separately.

One of the potential challenges in this kind of thermal treatment of biomass is to make it to the industrial scale and continuous process. The excessive amount of heat needed in the process makes this challenging and leaves little room for profitable business, thus, it needs thorough synergetic technical and economic research.

Acknowledgements

The authors would like to thank Auramo Foundation for funding this project.

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