Pre-treatment of coniferous biomass via hydrothermal carbonization and torrefaction: mass and energy yields

Sermyagina Ekaterina, Saari Jussi, Vakkilainen Esa

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ABSTRACT: Fuel properties of woody biomass could be significantly improved with several pre-treatment technologies. This paper presents the results of experimental comparison of hydrothermal carbonization and torrefaction processes for coniferous wood chips. Hydrothermal carbonization was performed within the typical reaction temperatures 180 – 250 °C during six hours. In torrefaction tests, the biomass was kept in an inert atmosphere for 30 minutes at temperatures 240 - 300 °C. Mass and energy yields of pre-treated biomass were calculated for all experimental sets. Within the limits of selected operation parameters, HTC demonstrated more intensive decomposition of feedstock comparing to torrefaction, and with higher mass losses resulted in lower values of energy yields than in case of torrefaction. Keywords: biomass; pre-treatment; energy densification.

1 INTRODUCTION

The pursuit to overcome the environmental problems together with depletion of fossil fuel sources broaden the range of available technologies for energy generation [1-3]. Bioenergy presents rather attractive alternative to substitute the fossil fuels: produce energy and vehicle fuels as well as various chemicals from renewable sources. According to the statement of European Union (EU) Commission [4], biomass, particularly wood and wood by-products, is expected to be the main contributor to the renewable energy targets determined by EU Renewable Energy Directive [5].

Among EU Member States, Finland with around 73% of land covered by forest is among the leaders in utilizing bioenergy, mainly represented by woody fuels [6]. The share of renewables in gross final consumption of energy in Finland accounted for 32.2% in 2010 [7] with target of increasing up to 38% to 2020 [8]. The largest share of wood-based fuels (wood chips and forestry by-products) use is concentrated in combined heat and power production (68%), followed by district heating (22%) and domestic use (10%) [9].

Heat and electrical energy could be produced from biomass through thermo-chemical treatments, in most cases, combustion and gasification [1]. However, untreated woody biomass is hardly competitive with fossil fuels. A relatively high moisture content, low energy density, poor grindability and heterogeneity of chemical and physical properties – these properties increase transport and handling costs for biomass fuels [10-15]. Several pre-treatment steps could be applied to improve fuel characteristics and increase potential of applications for biomass, namely: co-firing in coal-fired power plants and gasification [16-21]. Current work compares two promising technologies for biomass upgrading: hydrothermal carbonization (HTC) and torrefaction.

In hydrothermal carbonization, biomass is heated for several hours in a mixture with water at the temperatures 180 – 250 °C [10, 22-26]. Generated pressures correspond to saturated values. Reaction temperature together with residence
time and a ratio between water and biomass are the main factors determine the rate of carbonization of feedstock material [10, 25, 26]. As for torrefaction, this treatment is presented by slow heating of biomass in an inert atmosphere. Typical reaction temperatures are ranging from 200 °C to 300 °C [13, 16, 17, 23]. The reaction temperature and time strongly influence the process performance [17]. Additionally to solid product, the process produces a combustible gas as a side product [16, 17].

Both pre-treatments result in certain structural changes in main components of woody biomass (hemicellulose, cellulose and lignin). Generated solid materials, usually referred as hydrochar in case of HTC and torrefied wood in case of torrefaction, gain some similar properties: solids are more brittle, hydrophobic, homogeneous and have higher energy density in comparison with feedstock [11-14, 16, 17, 22, 25]. Reaction mechanisms of decomposition during HTC and torrefaction follow the similar pathways [11]. Hemicellulose is mainly decomposed as the most reactive component, followed by partial depolymerization and decomposition of cellulose and thermal softening of lignin [16, 27, 28]. It is reported that these processes in case of torrefaction become more pronounced at temperatures higher than 250 °C [17, 19]. In case of HTC, hydrolysis of hemicellulose and cellulose to monosaccharides is reported to be a dominant reaction accompanied by dehydration, decarboxylation and aromatization. In addition, lignocellulosic components become more reactive in the presence of water under saturated conditions: hemicellulose is easily hydrolyzed already at 200 °C, and the decomposition of more stable cellulose already occur at lower than in torrefaction temperature range (230 – 260 °C) [10-12, 23, 29].

Results of torrefaction treatment for some coniferous species are currently available in literature: larch [19], pine [16, 18, 23, 30], spruce [15, 16, 31], logging residue chips [30] and fuel tree chips [15]. As for HTC, the experiments with coniferous wood are currently limited to pine [23, 32] and white fir/Jeffrey pine mix [21]. Certain structural differences in wood cell components for deciduous and coniferous wood lead to different character of their decomposition [16, 17]. Consequently, as far as coniferous wood is concerned, more knowledge is needed for comprehensive evaluation of these pre-treatment steps. The feedstock material was subjected to the treatments under typical reaction conditions, and mass and energy yields for pretreated solids were calculated. The aim of current study is to compare the capability of hydrothermal carbonization and torrefaction for energy densification of coniferous wood chips.

2 MATERIALS AND METHODS

2.1 Feedstock material

Wood chips from pine and logging residues collected locally (Lappeenranta, Finland) were used for experiments. The feedstock material was milled to the particle size of 1 cm in length on average and air dried. Before the experiments biomass was kept in plastic bags at room temperature.
2.2 HTC reactor and procedure

Hydrothermal carbonization was carried out in a tubular reactor (Figure 1) designed and constructed at Lappeenranta University of Technology. The reactor is made from a stainless steel tube of 1 l inner volume with a flange connection at the top part and screw closing at the bottom. Experimental unit was indirectly heated by a 10 kW electric heater coil, and protected from undesirable heat losses by thick insulation layer. Thermocouples measured the temperature inside the reactor. Pressure sensor and pressure relief valve were installed at the top of the unit. The required temperature level inside the reactor during desired period of time was maintained with proportional-integral-derivative (PID) controller.

In current HTC experiments, approximately 50 g of biomass was dispersed in 300 ml of water, stirred manually, and then loaded into the reactor. In literature, the residence time varies from 30 min [32-34] for non-lignocellulosic materials to several hours [20, 22, 24, 25, 35, 36] for lignocellulosic. In current work, residence time of six hours was chosen to ensure the complete carbonization. After cooling to room temperature, the hydrochar and liquid product were collected and separated by vacuum filtration using the Büchner funnel with Whatman glass microfiber filter paper (grade GF/A). Hydrochar was subsequently dried overnight in the oven at a temperature of 105±2 °C and kept in plastic bags for further analysis. All tests were performed at least twice and the average value was chosen. Liquid and gaseous products analysis was not included in the scope of the current work.

Hydrochar samples were named in accordance with the process temperature as HTC-\(T\), where \(T\) denotes the reaction temperature.
2.3 Torrefaction reactor and procedure

For torrefaction experiments, the vertical quartz glass tube with the grid in the middle was used instead of steel reactor described above. Figure 2 presents the instrumentation diagram for torrefaction installation.

In order to obtain an inert atmosphere during experiments, constant gas flow of nitrogen (0.5 l/min) was introduced at the bottom part of reactor and maintained by Bronkhorst mass flow controllers during the experiments. Torrefaction gas passed through the filter and cooler and could be then directed to gas analyzer (Thermo 60i or Servomex 5200 MP) for gas composition analysis (gas analysis was not included in a scope of current work). The temperature distribution was monitored with two thermocouples above and below the grid. Required temperature inside the reactor was maintained with PID controller on necessary level during the desired period of time.

Figure 2. Instrumentation diagram of torrefaction reactor.

For torrefaction experiments, about 7 g of biomass was introduced into the reactor and the nitrogen was blown through the reactor for several minutes to purge the oxygen out of the system. In order to investigate high temperature torrefaction, sample was then heated up to the desired temperature in the typical range of 240 °C and 300 °C [17, 19]. The residence time at reaction temperature was set on the level of 30 minutes. Residence time was chosen on the basis of published results [16, 30, 31]. Gaseous products analysis was not included in this work. Torrefied biomass samples were named according to the process parameters as Torre-\(T\), where \(T\) denotes the reaction temperature.

3 ANALYTICAL METHODS

Untreated biomass was characterized by proximate analysis according to standard procedures. The heating values of both raw and pre-treated biomass samples were measured. Each sample was analyzed at least twice, and the average value was chosen.
3.1 Proximate analysis

According to the standard SFS EN 14775:2009 [37], the percentage of ash in solid biofuel could be found as a mass of inorganic residual after heating the sample to temperature 550 °C in air under controlled time and temperature conditions. The mass loss of biomass sample after keeping at the temperature of 900 ± 10 °C during seven minutes without contact with air refers to volatiles [38]. The moisture was determined with the moisture meter Sartorius 7093. Fixed carbon content was then calculated as a difference between 100% and sum of the percentages of moisture, volatile matter and ash content.

3.2 Heating value

Higher heating value was measured with the Parr 6400 calorimeter in accordance with standard [39]. Fuel sample (approximately 0.5 g) was ground to powder and pelletized with a pellet press. Sample pellet is then placed in a nickel crucible and ignited by a pure cotton fuse. The temperature increase in the water jacket that surrounds the calorimeter is used for the higher heating value calculation.

4 RESULTS AND DISCUSSION

4.1 Biomass characterization

The results of proximate analysis and the higher heating value for feedstock material are presented in Table 1. High volatiles content and low ash content are quite typical for woody biomass [1, 40, 41].

<table>
<thead>
<tr>
<th>Material</th>
<th>Proximate analysis [wt%]</th>
<th>Heating value [MJ/kg]</th>
<th>HHV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
<td>Ash</td>
<td>Volatiles</td>
</tr>
<tr>
<td>Wood chips</td>
<td>8,00</td>
<td>0,74</td>
<td>82,6</td>
</tr>
</tbody>
</table>

4.2 Mass and energy yields

The following equations for mass yield (MY) [%], energy yield (EY) [%] and energy densification ratio (ER) [-] were used in this study for analysis of experimental results:

\[
MY = \frac{m_{\text{solids, out}}}{m_{\text{solids, in}}} \cdot 100\% \quad (1)
\]

\[
ER = \frac{\text{HHV}_{\text{fuel, out}}}{\text{HHV}_{\text{fuel, in}}} \quad (2)
\]

\[
EY = MY \cdot ER \quad (3)
\]

where \(m_{\text{solids, in}}\) [kg] is the dry mass of feedstock used for the experiment, \(m_{\text{solids, out}}\) [kg] is the dry mass of pre-treated biomass after the experiment, \(\text{HHV}_{\text{fuel, out}}\) [MJ/kg] is the higher heating value of pre-treated wood (dry basis), \(\text{HHV}_{\text{fuel, in}}\) [MJ/kg] is the higher heating value of feedstock material (dry basis).

Hydrochar samples after treatment at the highest temperature (250 °C) had dark black color, while biomass after
torrefaction at 300 °C had certain amount of brown color the particles. This color change difference implies that hydrothermal carbonization treatment within studied process parameters resulted in more complete decomposition of biomass components in comparison with torrefaction.

Resulting mass and energy yields together with relative increase of higher heating value for biomass after treatments are presented in the Table 2.

The reaction temperature has a notably strong effect on biomass decomposition in both pre-treatment techniques: higher mass losses of feedstock material occur with temperature increase. Mass yield for HTC varies from 67.16% at the lower temperature limit to 51.85% at the higher one. Such numbers are quite typical for HTC treatment of coniferous wood species [21, 23]. In case of torrefaction, the mass yield decreases from 88.33% to 66.62% over studied temperatures. The tendency is consistent with available literature for coniferous biomass torrefaction [23, 30, 31].

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Sample name</th>
<th>MY [%]</th>
<th>ER [-]</th>
<th>EY [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermal carbonization</td>
<td>HTC-180</td>
<td>67,16</td>
<td>1,13</td>
<td>75,88</td>
</tr>
<tr>
<td></td>
<td>HTC-200</td>
<td>60,18</td>
<td>1,21</td>
<td>72,54</td>
</tr>
<tr>
<td></td>
<td>HTC-220</td>
<td>56,91</td>
<td>1,29</td>
<td>73,22</td>
</tr>
<tr>
<td></td>
<td>HTC-240</td>
<td>52,83</td>
<td>1,36</td>
<td>72,08</td>
</tr>
<tr>
<td></td>
<td>HTC-250</td>
<td>51,85</td>
<td>1,40</td>
<td>72,79</td>
</tr>
<tr>
<td>Torrefaction</td>
<td>Torre-240</td>
<td>88,33</td>
<td>1,00</td>
<td>88,13</td>
</tr>
<tr>
<td></td>
<td>Torre-260</td>
<td>82,45</td>
<td>1,01</td>
<td>83,42</td>
</tr>
<tr>
<td></td>
<td>Torre-280</td>
<td>75,52</td>
<td>1,03</td>
<td>77,89</td>
</tr>
<tr>
<td></td>
<td>Torre-300</td>
<td>66,62</td>
<td>1,06</td>
<td>70,35</td>
</tr>
</tbody>
</table>

Hydrothermal carbonization significantly increases biomass energy content: the higher heating value of hydrochar at 250 °C is 40% higher than feedstock material. Relatively the same values are reported in [21, 23]. Within the range of investigated parameters, torrefaction results in more moderate rates of energy densification: with 6% heating value increase after the treatment at 300 °C. The tendency observed is consistent with some published materials for coniferous biomass [15]. Differences in process conditions and feedstock materials result in somewhat higher values for energy densification that could be found in works of [18, 23, 30].

Energy yield value is influenced by two factors acting inversely with temperature growth: decreasing mass yield and increasing energy densification ratio. In case of hydrothermal carbonization, these two factors are almost balanced each other, and for this reason, the energy yield decreases slightly with temperature: the average value over the temperature range is 73.3%. Quite comparable results are presented for loblolly pine in [23, 32]. As for the torrefaction, under the influence of decreasing mass yield, the energy yield value varies from 88.13% at 240 °C to 70.35% at 300 °C. Such tendency is consistent with the published data for coniferous biomass [15, 16, 30, 31].

Within the range of investigated parameters, hydrothermal carbonization resulted in higher extent of biomass decomposition (more significant mass losses and increase of heating value) comparing to torrefaction. At the same time, torrefaction treatment with studied settings leads to a higher energy yields. On the other hand, it should be noted that the process conditions define to a considerable extent the performance of the process. In experiments published by Wei et al. [23], reaction times were significantly different than in current study (80 min for torrefaction, and around 5 min for HTC), and as a result, hydrothermal carbonization demonstrated the higher values of energy yields (with somewhat lower mass
losses) than torrefaction (with higher increase of heating value).

5 CONCLUSIONS

Bioenergy has a significant potential to increase the share of renewables in energy generation. Several pre-treatment technologies could be applied for solving certain problems associated with wood-based fuels. Torrefaction and hydrothermal carbonization are two promising pathways that imply to thermal treatment of biomass to improve the fuel properties. Decomposition of wood cell components that take place during these processes, converts the biomass into a value-added product: it becomes more brittle, the ability to absorb moisture is decreased while the energy content is increased.

In the current work, two pre-treatment technologies for coniferous wood chips are compared. In hydrothermal carbonization experiments, biomass in a mixture with water was treated during six hours within the temperature range between 180 – 250 °C. The decomposition reactions are intensified with temperature increase: mass yield of hydrochar varies between 67.2% and 51.9% at lower and higher temperature limits correspondingly. Torrefaction of wood chips during 30 minutes in absence of oxygen resulted in somewhat smaller mass losses: with mass yields of 88.3% at 240 °C and 66.6% at 300 °C. The relative increase of the heating value of treated biomass at the highest temperature in case of torrefaction is 6%, while the hydrochar heating value is 40% higher than the initial one. So, within the limits of selected reaction parameters, hydrothermal carbonization shows higher energy densification rates and more intensive decomposition of feedstock in comparison with torrefaction. At the same time, higher mass losses resulted in lower values of energy yields than in case of torrefaction: averaged over the temperature range, the energy yields for hydrothermal carbonization and torrefaction are 73.3% and 79.9%, respectively.

The results presented in this study confirm that hydrothermal carbonization and torrefaction could considerably increase the energy content of coniferous biomass. The process settings determine the extent of decomposition reactions occur during both processes and, as a consequence, the properties of pre-treated biomass. Optimal selection of reaction parameters defines the efficiency of biomass treatment. However, the overall efficiency of the process will be influenced by integration possibilities with other processes together with feedstock properties, and should be further investigated.

References

[7] Official Statistics of Finland: Share of renewable energy in gross final energy consumption,


