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# Guideline: Densification of torrefied biomass

Resultat Kontrakt (RK) Report

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# 1 INTRODUCTION

The market for solid biofuels i.e. wood pellets has grown from 2 million to about 18 million tons per year during the last decade. This development is going to continue especially since European power providers are under pressure from their governments to reduce the $CO_2$ emissions and to reduce the utilization of fossil fuels. The utilization of biomass in existing coal plants for heat and power production (CHP) is often seen as a relatively fast and cost efficient way to reduce the $CO_2$ emissions compared to other renewable alternatives such as solar power and wind energy. Other advantages are the high reliability of biomass firing that is independent of weather conditions and day time. Several CHP plants are using wood pellets as fuel and many more will be switched from coal to biomass in the coming years. The use of biomass in conventional CHP plants requires changes to be made to the plant. Power producers are therefore interested in biomass with properties similar to coal as possible and a competitive price at the same time.
Some properties of biomass are inconvenient for its utilization as fuel in combustion and gasification processes, i.e. its high oxygen contents, low calorific value, hydrophilic nature, and high moisture content (van der Stelt et al. 2011). Apart from these, its fibrous and tenacious structure, as well as its inhomogeneous composition, makes biomass even more challenging and energy-intense to process (van der Stelt et al. 2011).

Numerous studies have shown that torrefaction converts biomass into a fuel with favourable properties (Acharjee et al. 2011; Arias et al. 2008; Bourgois et al. 1989; Brosse et al. 2010; Deng et al. 2009; Kiel et al. 2008; Kleinschmidt 2011; Pentananunt et al. 1990; Pimchuai et al. 2010; Prins et al. 2006a-c; Repellin et al. 2010; Yan et al. 2009). However it has also been shown that torrefaction and densification of torrefied biomass into solid energy carriers is not straight forward. Different research projects on international level (i.e. EU-project SECTOR, EUDP project - Torrefaction Development and Demo Plant and the EFP project TOBRI) are working to solve the most important challenges related to densification of torrefied biomass.

The present report provides an overview of torrefaction and densification processes and reviews relevant literature that has been published during the last years. The report has been published by the Danish Technological Institute as a part of a review article in an international research magazine during the summer 2012: Stelte et al. Recent developments in biomass pelletization. Bioresources, 2012, 7(3):4451-4490.
The complete article is available free of charge on the journal website:
http://www.ncsu.edu/bioresources/BioRes_07/BioRes_07_3_4451_Stelte_SHAHS_Recent_Development_Biomass_Pelletization_Review_2992.pdf

# 2 TORREFACTION

Torrefaction is a thermal pre-treatment process in which the biomass is heated up to 200-300°C in the absence of oxygen (usually under nitrogen atmosphere). The resulting product has a lower oxygen content, higher calorific value, low moisture content, and less hydrophilic compared to the untreated biomass. Furthermore, the fibrous and tenacious nature of the biomass is reduced, resulting in a brittle material that can easily be comminuted into smaller particles (van der Stelt et al. 2011).
According to van der Stelt (2011) the torrefaction process can be subdivided into five stages

1. **Initial heating:** The temperature is increased until moisture starts to evaporate and drying of the biomass begins.

2. **Pre-drying:** At 100 °C the free water is evaporated from the biomass at a constant temperature
3. **Post-drying and intermediate heating:** Further heating of the biomass to about 200 °C
4. **Torrefaction:** During this stage the actual torrefaction process takes place. The temperature is further increased to about 270 to 310 °C and the biopolymers especially hemicelluloses are undergoing condensation and dehydration reactions resulting in the release of gas (torrefaction gas) and torrefied biomass.
5. **Solids cooling:** Cooling of biomass below 200 °C

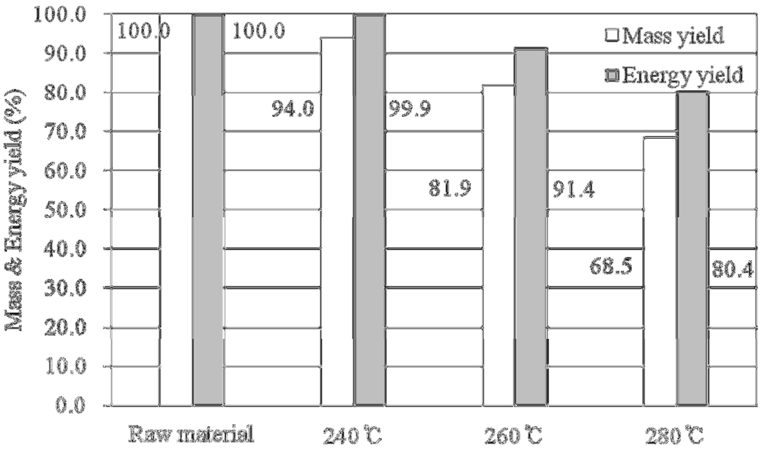

**Fig. 1.** Mass and energy yield for biomass torrefied at different torrefaction conditions (Kim et al 2012).

During torrefaction, the biomass is partly decomposed, in the process of which low molecular organic volatile compounds evaporate from the biomass (Prins et al. 2006b). This results in a decrease of mass, while the initial energy content is only reduced slightly. However as a consequence, the energy density of the biomass is increased, making it more attractive as a fuel (van der Stelt et al. 2011). Kim et al. (2012) have studied the mass and energy yield when torrefying yellow poplar at temperatures between 240 and 280°C (Fig. 1). The mass loss is greater than the energy loss, indicating that mainly volatiles of low energy density evaporate from the biomass during torrefaction. Shang et al. (2012) have correlated the heating value of torrefied biomass with the anhydrous weight loss (AWL) and energy loss, as shown in Fig. 2.

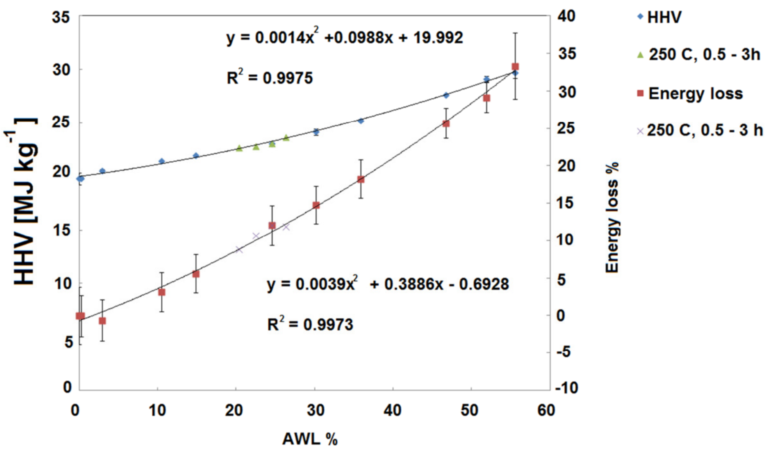

**Fig.2 .** Higher heating value (HHV) and percent of energy loss of wheat straw torrefied at different temperatures (150, 200, 220, 230, 250, 260, 270, 280, 290, 300°C) for 2 hours. The data points "250°C, 0.5-3 h" represent data at 250°C with residence times of 0.5, 1, 2, and 3 hours. The x-axes shows the anhydrous weigh loss (AWL) and the red bricks correspond to the increase in torrefaction temperature (150, 200, 220, 230, 250, 260, 270, 280, 290, 300°C) (Shang et al, 2012).

Torrefaction is used to convert various types of lignocellulosic biomass into an energy-dense homogeneous solid. The volatiles can be subdivided into condensable and non-condensable compounds. Condensable compounds are mainly water and organic acids, while non-condensables consist mainly of carbon monoxide and carbon dioxide (Prins et al. 2006b). Furthermore, biomass polymers, i.e. hemicelluloses, cellulose, and lignin, are degraded and/or transformed (Melkior et al. 2012). The most reactive compounds are hemicelluloses. Xylan was found to decompose quickly at about 200°C, resulting in high weight loss of the biomass. Cellulose degradation starts slowly at about 270°C, but accelerates noticeably at temperatures above 300°C (Prins et al. 2006a). Rousset et al. (2009) have studied the thermal degradation of lignin under torrefaction in great detail and concluded that lignins are more resistant to prolonged heat treatment than polysaccharides, and that lignin undergoes intense structural transformations during torrefaction, mainly cleavage and condensation reactions. Shang et al. (2012) have studied the chemical changes during torrefaction of wheat straw at temperatures between 150 and 300°C by means of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The spectra (Fig. 3) shows a degradation of hemicelluloses at relatively low torrefaction temperatures (starting at 250°C). Indications of the degradation of hemicelluloses is the gradual decrease of the carbonyl stretching band of carboxylic acid groups of hemicelluloses at 1732 cm-1 and the decrease of a band at 900 cm-1 that can be assigned to xylan, a major building block of hemicelluloses.

Bands assigned to cellulose (670 and 1160 $cm^{-1}$) decrease at temperatures above 270°C. Bands assigned to lignin (1505 cm-1) remain stable over the whole temperature range (Shang et al. 2012).

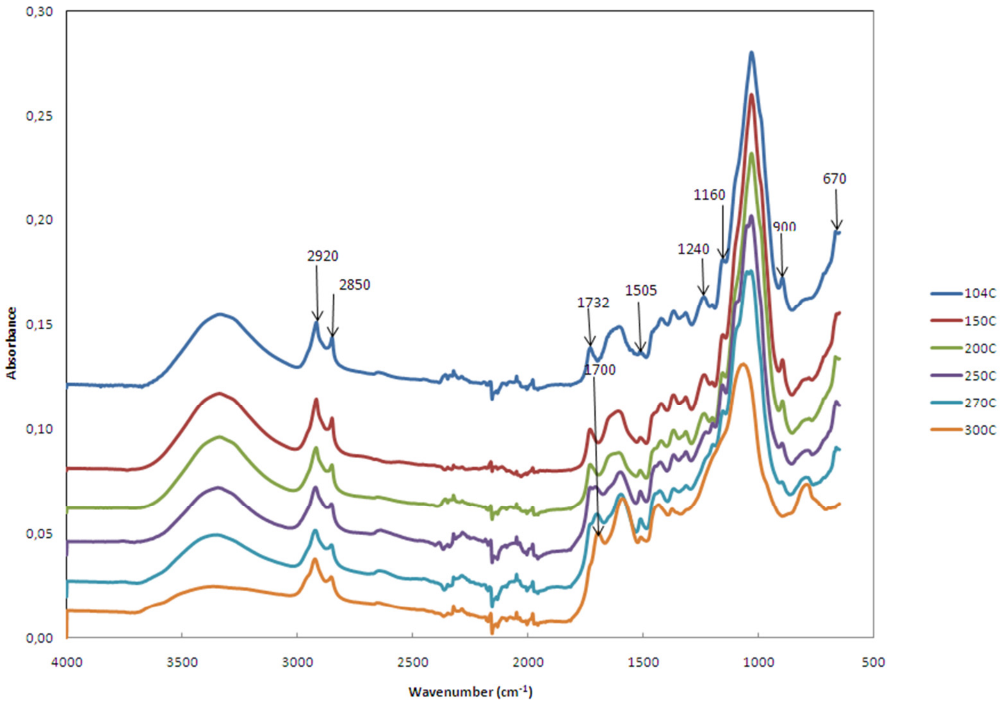

**Fig. 3**. ATR-FTIR spectra of oven dried (104°C) and torrefied wheat straw samples. All spectra are separated to ease comparison. (Shang et al., 2012)

Stelte et al. (2012b) conducted a standard fiber analysis of wheat straw torrefied at temperatures between 150 and 300°C in 50°C intervals (termed T150, T200, T250, T300). Their results support the finding that hemicelluloses are degrading at low temperatures, while cellulose and lignin (insoluble fraction) are more stable. The data is shown in Table 1. The high amount of insoluble residues for the T300 sample is probably due to thermal degradation products that interfered with the procedure used to quantify the lignin concentration (Yan et al. 2009).

**Table 1.** Fiber Analysis of Torrefied Wheat Straw (Data from Stelte et al. 2012b)

| Sample | Cellulose | Hemicellulose | Insoluble fraction | Ash | Yield [%DM] |
|---|---|---|---|---|---|
| Straw | 37.2 ± 0.3 | 27.3 ± 0.4 | 19.2 ± 0.5 | 4.9 ± 0.2 | 100 |
| T150 | 36.4 ± 0.4 | 27.1 ± 0.5 | 19.1 ± 0.6 | 5.5 ± 0.3 | 99.7 |
| T200 | 36.7 ± 0.4 | 26.1 ± 0.2 | 20.7 ± 0.5 | 5.4 ± 0.2 | 96.8 |
| T250 | 37.5 ± 0.2 | 5.8 ± 0.1 | 47.2 ± 0.3 | 6.7 ± 0.4 | 74.7 |
| T300 | 1.4 ± 0.2 | 4.6 ± 0.3 | > 80 | 10.7 ± 0.4 | 45.9 |

A detailed analysis about the chemical changes during biomass torrefaction has recently been published by Kim et al. (2012), where they studied the torrefaction process of yellow poplar. They conducted a fiber analysis and studied the condensate fraction as well as analysing the elemental composition and inorganic compounds at different torrefaction conditions. They found that hemicellulose contained in torrefied biomass decreased with increase in torrefaction temperature (240 to 280°C and 30 minutes reaction time); they observed only slight effects on the cellulose and lignin content in the biomass.

Torrefaction improves the combustion properties, since higher combustion rates can be achieved while reducing smoke emissions at the same time. Different studies have been conducted to investigate the grinding of torrefied wood (Pentananunt et al. 1990; Arias et al. 2008; Repellin et al. 2010; Shang et al. 2012). Both grinding energy and product particle size were decreased with torrefaction. The biomass gets completely dry during torrefaction. Due to the degradation of the carbohydrate polymers (dehydration reactions) most of the hydroxyl groups that can act as bonding sites for water, are removed from the biomass. Hence, the hygroscopic nature of biomass is partly lost (Bergman 2005). Stelte et al. (2011a) investigated the water uptake of torrefied spruce by exposing it to 250, 275, and 300°C air with a relative humidity of 65, 75, and 90%. The results summarized in Fig. 4 show that torrefied spruce absorbs less water than untreated wood.

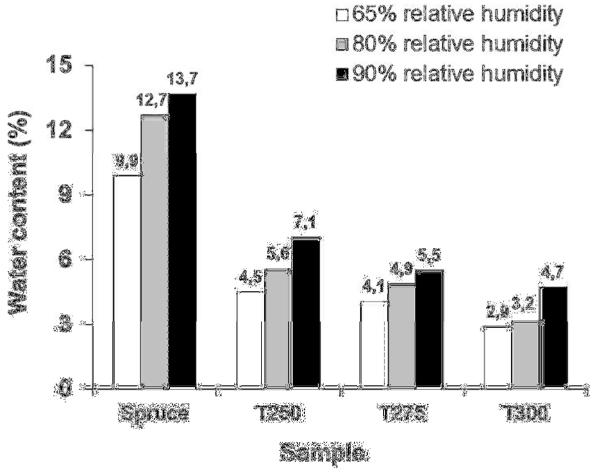

**Fig. 4.** Moisture content of spruce and torrefied spruce after three weeks of storage in climate chambers at 65, 80 and 90% relative humidity and 27°C. (Stelte et al. 2011a)

## 3 DENSIFICATION

Recently, torrefaction has been combined with pelletization to produce a biofuel with "coal like" properties; this process is advantageous when it comes to substitution and/or supplementation of coal with biomass in coal-based power plants. Main advantages are better grinding properties and storage properties when compared to conventional wood pellets. Torrefied pellets contain less moisture, have a higher heating value, and are less sensitive to moisture uptake and biological degradation (i.e. fungi and bacteria). Furthermore they can be ground into a dust like powder using conventional coal mills while wood pellets require a special mill and higher energy input for grinding (Kleinschmidt 2011).

So far only a few studies have been published about the pelletizing properties of torrefied biomass (Bergman 2005; Li et al. 2012, Pirraglia et al. 2012, Stelte et al. 2011a, 2012b; van der Stelt et al. 2011). There are somewhat opposing opinions on whether torrefaction has a positive or negative effect on pelletizing properties and quality.

Some studies claim that torrefaction improves the mechanical properties of the biomass pellets because of its high lignin content (due to thermal degradation of hemicelluloses and cellulose) (Kiel et al. 2008; van der Stelt et al. 2011), while other studies indicate that the mechanical properties of pellets obtained from torrefied biomass are lower (Gilbert et al. 2009; Li et al. 2012, Stelte et al. 2011a). It has been shown earlier that the thermal softening of lignin and its subsequent flow results in inter-penetration of amorphous polymer molecules between adjacent biomass particles, and this is likely to have a great effect on pellet strength (Stelte et al. 2011d, 2012a).

Nevertheless, a high lignin content does not necessarily mean better bonding, especially since the low moisture content of the biomass has been shown to influence the softening temperature of the lignin, and as such, the bonding properties of the biomass (Stelte et al. 2011c). Some studies indicate that the softening temperatures of dry lignin are well above the typical temperatures reached in the pelletizing processes (Kelley et al. 1987; Olsson and Salmen 1992).

There are studies regarding the pelletizing process which suggest that torrefaction significantly reduces the energy used for pelletization due to the reduced energy required for grinding the material and lower pressures required for pelletization (Bergman 2005). On the other hand, another study indicated increased friction within the press channels of a mill when pelletizing torrefied biomass (Stelte et al. 2011a), likely due to the absence of lubricating extractives and amorphous polymer molecules. The results indicate that the friction in the press channel of a pellet mill increases with increase in torrefaction temperature and that the pellet's mechanical properties and density decrease with increase in torrefaction temperature. This is possibly due to less extractives and polymer molecules being present on the surface. Li et al. (2012) reported significantly higher energy consumption for compaction and extrusion processes of torrefied sawdust from spruce and fir compared to untreated material. They explained the increase due to a decrease of particle plasticity during torrefaction due to thermal decomposition of lignin and hemicelluloses into organic acids, sugars, and charcoal.

Decreasing the mechanical properties of the torrefied biomass can be beneficial when it comes to comminuting biomass pellets to dust prior firing, i.e. conventional coal mills might suffice. Lower pellet stability may result in problems during transport and handling due to the formation of dust and fines. Therefore, a compromise between good grinding properties and sufficient stability during pellet handling has to be found. Studies (Stelte et al. 2011a, 2012b) indicate that torrefaction temperatures of about 250°C result in stable pellets of high energy density and favourable mechanical properties during size reduction and milling processes. Increase in the torrefaction temperature increased the amounts of defects, as shown in Fig. 5; torrefaction temperatures higher than 250°C results in a material where pellets cannot be formed.

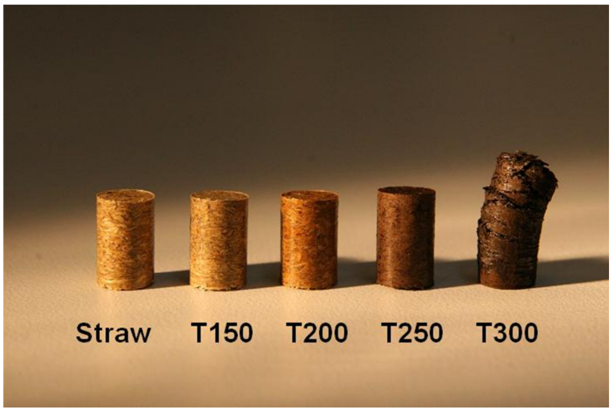

**Fig. 5.** Pellets made from torrefied wheat straw. From left to right: Untreated straw and torrefied straw at 150, 200, 250 and 300°C (Stelte et al 2012b).

In another study (Stelte et al. 2011a), the compression strength of the pellets made from spruce torrefied at 250, 275, and 300°C were compared among each other and to untreated spruce (Fig. 6). The results indicated that the compression strength decreases with an increase in torrefaction temperature. At very high torrefaction temperatures (300°C) it was not possible to pelletize the obtained biomass.

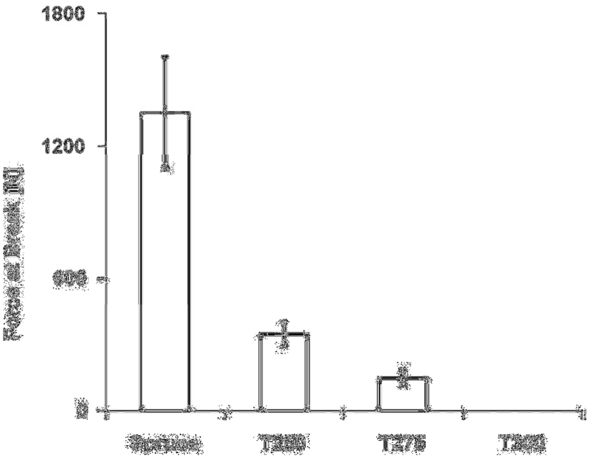

**Fig. 6.** Compression strength of spruce pellets compared to pellets made from torrefied spruce (Stelte 2011a).

Li et al. (2012) studied the pelletizing properties of torrefied sawdust made from a mixture of spruce and fir. The authors report both a decrease of pellet density and Meyer hardness for pellets made from torrefied wood. Density and hardness decrease with an increase in torrefaction temperature, as shown in Fig. 7.

Apart from the torrefaction temperature, time seems to be a crucial factor. The combination of torrefaction temperature and time influence the final biomass composition and thereby influence its pelletizing properties. Nordwaeger et al. (2010) conducted a parametric study of pilot-scale biomass torrefaction and have found that the torrefaction temperature generally affects the properties of the product more than the torrefaction time.

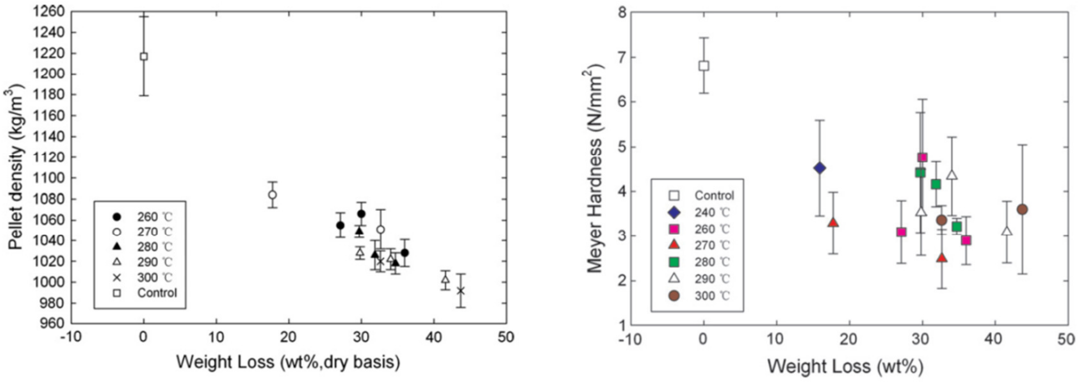

**Fig. 7.** a) Pellet density of pellets pressed from torrefied sawdust as a function of weight loss and torrefaction temperature. b) Meyer hardness of torrefied pellets as a function of torrefaction temperature and residence time (Li et al. 2012).

Alternative heat treatment processes have also been considered. A recent study by Lam et al. (2011) suggests that steam explosion of wood results in a material with favorable fuel properties (high heating value, low moisture absorption) and good pelletizing properties. Their manufactured pellets do not show any defects (Fig. 8) and pellet density increases. Similar results have been obtained by Biswas et al. (2011) who studied the pelletizing properties of steam exploded salix. It was found that steam explosion treatment reduced the amount of alkali metals in the biomass, and the pressed pellets showed an increased density, impact and abrasion resistance. Nevertheless, small decreases in ash fusion characteristics and char reactivity was reported for elevated temperatures and residence times.

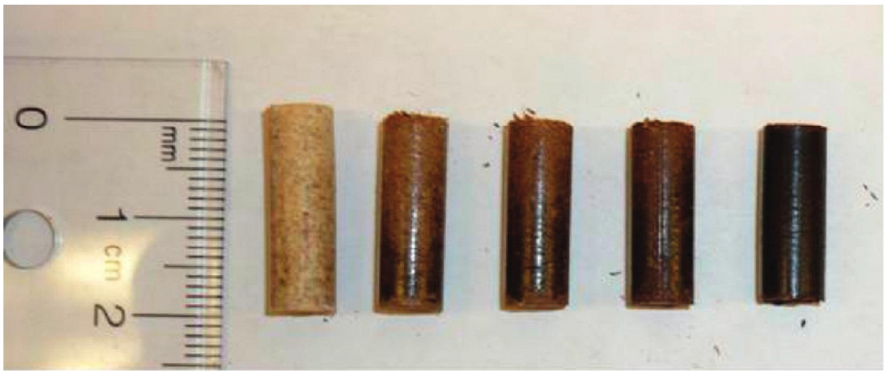

**Fig. 8.** Physical appearance of wood pellets treated at different steam explosion conditions. From left to right: untreated, 200°C for 5 min, 200°C for 10 min, 220°C for 5 min, and 220°C for 10 min (Lam et al. 2011).

Reza et al. (2012) have used hydrothermal carbonization (HTC) as a pretreatment process for making pelletized biomass more homogeneous and energy dense. HTC is a process where biomass is treated with hot compressed water in the temperature range between 200 and 260°C. The resulting biomass had an increased lignin content that acted as binder in the subsequent pelletization step. The resulting pellets had a higher energy and mass density and favorable physical properties (i.e. moisture resistance, mechanical stability). The pellet surface was studied by means of scanning electron microscopy and compared to pellets made from untreated and (dry) torrefied samples. It was shown that the pellets made from untreated and HTC treated biomass had a more compact structure and exhibited good inter-particle bonding. Pellets made from torrefied biomass showed cracks and had inferior mechanical properties. HTC treatment involves pressurized conditions and thus the process equipment is more costly and complicate compared to conventional torrefaction reactors (Hoeckman et al. 2011). Therefore, it is necessary to have a close look on mass and energy balances of the process and to investigate whether the material properties justify higher operation and investment costs. Hoeckman et al. (2011) suggest that a two-step HTC process involving low- and high-temperature treatment might both maximize the recovery of sugars and the production of an energy dense biomass char.

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