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Changes of chemical and mechanical behavior of torrefied wheat straw

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Abstract

The purpose of the study was to investigate the influence of torrefaction on the grindability of wheat straw.
Straw samples were torrefied at temperatures between 200 °C to 300 °C and with residence times between 0.5 to 3 hours. Spectroscopic information obtained from ATR-FTIR indicated that below 200 °C there was no obvious structural change of the wheat straw. At 200-250 °C hemicelluloses started to decompose and were totally degraded when torrefied at 300 °C for 2 hours, while cellulose and lignin began to decompose at about 270-300 °C. Tensile failure strength and strain energy of oven dried wheat straw and torrefied wheat straw showed a clear reduction with increasing torrefaction temperature. In addition, Hardgrove Grindability Index (HGI) of wheat
straw torrefied at different conditions was determined on a standard Hardgrove grinder. Both results showed an improvement of grindability in the torrefaction temperature range 250-300 °C, which can be well explained by the findings from FTIR analysis. At a torrefaction temperature of 260 °C and with a residence time of 2 hours, wheat straw samples produced similar HGI values as coal (RUKUZN) with 0% moisture content. Under this condition, the Anhydrous Weight Loss (AWL%) of the wheat straw sample was 30% on dry and ash free basis (daf), and the higher heating value of the torrefied wheat straw was 24.2 MJ kg⁻¹ (daf). The energy loss compared to the original material was 15% (daf).

Keywords: torrefaction, grindability, tensile strength, Hardgrove, ATR-FTIR, *Triticum aestivum* L.

1. Introduction

One of the drawbacks of using biomass as a fuel source is the fact that it is more tenacious and less brittle and hence more difficult and energy intensive to grind into fine particles. This problem is especially acute when biomass is to be used in pulverized combustion systems [1]. Torrefaction is a mild temperature (200-300 °C) pretreatment of biomass in an inert atmosphere, which has received increased attention in recent years [2]. During the process, the biomass looses moisture and a proportion of the volatile content, and becomes dry, darker, and brittle. Torrefied biomass is hydrophobic, has a higher calorific value and is easier to grind [3,4]. At present, a number of studies on grindability of torrefied biomass have been carried out. Arias et al. [3] ground torrefied eucalyptus wood in a cutting mill with a bottom sieve of 2 mm. In all cases, there is an improvement in the grindability characteristics of the treated biomass, as the percentage of particles passing to the lower size fractions greatly increases for the samples subjected to the torrefaction process. Bridgeman et al. [5] measured the Hardgrove Grindability Index (HGI) of willow heated at 240 °C and 290 °C for 10 and 60 minutes by using a Retsch ball mill. The higher temperatures and longer residence times improved the grindability. Abdullah and Wu [6] investigated the thermal pre-treatment (300-500 °C) of mallee wood in a fixed-bed reactor. A laboratory ball mill was used for testing the grindability. They found that thermal treatment below 330 °C leads to
significantly better grinding properties and that further temperature increase had only minor effects. Further studies about the torrefaction and grindability of wood samples have been made by [7-10].

Where these studies have shown the beneficial effect of torrefaction of woody biomass, grass samples such as wheat straw present more difficulty. Wheat straw has some unique properties that differ from woody biomass. The tenaciousness of the untreated wheat straw makes it almost impossible to grind in a ball mill, where the tumbling action rather flattens the fibers instead of crushing and breaking them. This is related to the ultra structural differences of the cell wall of wheat straw as compared to woody biomass. For example, wheat straw fiber has a much thicker outer layer in the secondary cell wall based on volume percentage compared to spruce tracheid. The fibrils in this layer are oriented laterally in cross helix making the defibrillation of grassy biomass more difficult [11]. From a chemical point of view, there is also difference between wheat straw and woody biomass. The main hemicelluloses found in hardwood are partially acetylated (4-O-methyl-D-glucuronopyranosyl)-D-xylans, while hemicelluloses in wheat straw are more complex, mainly consisting of a (1→4)-linked β-D-xylan with D-glucopyranosyluronic acid (or 4-O-methyl-α-D-glucopyranosyluronic acid) groups attached at position 2, and L-arabinofuranosyl and D-xylopyranosyl groups attached at position 3. They form hydrogen bonds with cellulose, covalent bonds (mainly α-benzyl ether linkages) with lignin, and ester linkages with acetyl units and hydroxycinnamic acids. The cross-linking of hemicelluloses and lignin by ferulates/diferulates in the wheat straw cell wall enhanced the difficulty of separating these two components [11]. Higher percentage of hemicelluloses in wheat straw compared with woody biomass also contributes to the better linkage between the polymers.

In studies of heat-induced modifications of biomass properties, Svoboda et al. [12] summarized that the main changes in biomass due to torrefaction involve decomposition of hemicelluloses and partial depolymerization of lignin and cellulose. Bella et al. [13] heated American hardwoods to temperatures between 200 °C and 400 °C, and found a lower cellulose and hemicelluloses resistance compared to lignin. Although some decomposition
temperatures for these compounds can be found in literature [5,8], there is a lack of experimental data indicating the close relationship between the thermochemical and the grindability changes, especially for wheat straw.

In the present work the heat-induced chemical modifications of biomass is monitored by Attenuated Total Reflectance (ATR) – FT-IR spectroscopy, where the samples were heated before recording the spectra. ATR-FTIR spectroscopy is a facile method which provides direct information from the outer (μm) sample surface layers with no requirement for prior sample preparation. The spectra recorded provide basic and in principle quantitative information on the sample cell wall polymers and their chemical modifications. These modifications, obtained at various torrefaction temperatures, are related to the mechanical and grindability properties. Different methods have been used to study these properties. One example is the Hardgrove Grindability Index (HGI), which in principle is a simple measure of grindability.

The HGI was developed as a measure, which indicates how difficult it is to grind a specific coal to the particle size necessary for effective combustion in a pulverized coal fired boiler [14]. In the standard method the HGI value is based on the amount of sample passing through a 75 μm sieve after being ground in a standard Hardgrove ball mill for 377 radians for each fixed amount of feed (50 g). Joshi [15] and Agus and Waters [16] pointed out that the fixed mass approach is unsatisfactory for making direct comparisons among fuels with densities differing a lot. To correct this situation and to bring evenness in grindability ratings of biomass and coal, Bridgeman et al. [5] used the same fixed volume (50 cm³) for each feed as opposed to a fixed mass (50 g).

As the HGI is based on an empirical method, it is not linked directly with any specific physical property of the sample, and suffers from relative low reproducibility and repeatability. Therefore, as a supplement, it was decided to investigate the tensile strength of the wheat straw samples before and after torrefaction. The tensile strength is the maximum stress that a material can withstand while being pulled before breaking. Furthermore, by measuring the elongation of the specimen while pulling it apart, it is possible to calculate the strain energy at fracture per unit volume. Yigit [17] related the energy absorbed per unit new surface area created during
comminution and the strain energy per unit volume of a solid at fracture, and established mathematical models assuming fracture by tensile stresses. Mathematical models of new surface area energy derived from different fracture patterns all have a positive linear relationship with strain energy per unit volume, if the starting particle size and the reduction ratio are constants. Although the models cannot fully represent the realistic fracture pattern of a comminution process, they allow one to use the relative change of the strain energy at fracture under tensile stress at different torrefaction temperatures as an indication of how much energy can be saved during grinding under the same mill conditions.

The objective of this study was to obtain knowledge on the effects of the torrefaction process on the chemical and mechanical behavior. Attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectroscopy, together with chemical analysis of cell wall composition were used to qualitatively determine the chemical changes in the lignocellulosic material during the torrefication process. HGI and tensile strength test were used to study the mechanical behavior of the straw at different conditions of torrefication. Higher heating value (HHV) was determined to establish a relationship between energy loss and anhydrous weight loss (AWL).

2. Material and methods

2.1. Torrefaction

The wheat straw used in this study is from winter wheat (Triticum aestivum L.), which was the most grown wheat species in Denmark in 2008. The straw was cut by hand in the field on the island of Funen, Denmark (55°21′N 10°21′E) in August 2008, and stored indoors packed in the paper bags. Prior to the experiment, wheat straw were selected and cut to about 30 cm long pieces. Samples were first dried in the oven at 104 °C for 24 hours, and then placed in an air tight metal container (15×31×10 cm) that could be heated in an oven (Lyngbyovnen of type S 90, 3 × 380 V, 9 kW) to the desired torrefaction temperature. 0.5 dm$^3$ min$^{-1}$ of nitrogen was pumped through the sample container to create an inert atmosphere. The temperature of the oven was measured in the centre of the chamber using thermocouples and this measurement was used for temperature.
control. The residence time of the torrefaction process starts when the material temperature has reached the set
temperature until it starts to cool down. Torrefaction was carried out at 150, 200, 220, 230, 250, 260, 270, 280,
290 and 300 °C with residence time of 2 hours. Additional different residence times of 0.5, 1, 2, 3 hours were
tested at 250 °C.

2.2. ATR-FTIR

For sample preparation wheat straw were comminuted in a Hardgrove ball mill and the particle size fraction
between 250-600 µm was used for the FTIR test. Before the test, these particles were dried in the oven at 40 °C
for 24 hours. ATR-FTIR spectra (4000-650 cm⁻¹) were recorded using a Fourier transform infrared spectrometer
(Nicolet 6700 FT-IR, Thermo Electron Corporation, USA). The system was equipped with a thermostat
controlled ATR unit (T = 30 °C) where the sample was pressed against the diamond surface using a spring-
loaded anvil. All spectra were obtained with 128 scans for the background (air) and 100 scans for the sample
with a resolution of 4 cm⁻¹ from 500-4000 cm⁻¹. Spectra were recorded from 10 different sub-samples for each
sample condition, and these spectra were normalized at around 690 cm⁻¹ where the spectra are free of distinct IR
bands. The average spectrum of the 10 normalized spectra was presented for each sample condition. A spectrum
was also obtained for each of the two xylans (from Birchwood and from oat spelts, both from Sigma) reference
samples (results not shown in this paper).

2.3. Tensile strength

Plant leaf materials were removed from the stem internodes, and a flat thin piece was cut from the hollow stem.
The ends of the specimens were glued between 2 pieces of aluminum by using ‘Loctite super glue, precision’
(Henkel, USA). The length of the specimen was in the range of 3-6 cm, and the width of the specimen was in the
range of 1.4-3.1 mm.

Tensile tests of wheat straw torrefied at different temperatures were tested using a tensile tester (Vantage,
Thwing Albert, USA) with a video extensometer measuring the prolongation of the straw. The elongation rate
was 1 mm min$^{-1}$ and stress was recorded using a 250 N load cell. Data from samples that failed close to the aluminum tabs were rejected. Each measurement was repeated 4 times, except for wheat straw torrefied at 300°C. Due to the brittleness of the sample, data were collected from only 2 samples. The tensile failure stress (or ultimate tensile strength), $\sigma$, of the specimen was calculated from the Eq. (1) [18]:

$$\sigma = \frac{F_t}{A}$$  \hspace{1cm} (1)$$

Where $F_t$ is the tension force at failure and $A$ is the area of the specimen at the failure cross-section. The cross-section area was measured both by an electronic digital micrometer (Digital Micrometer DIN 863, Diesella, Denmark) and calculated from the apparent density by assuming a uniform wall area and structure with length. The length and weight of each specimen were measured before the test, and the cross-section area was calculated as given in Eq. (2):

$$Area = \frac{m}{\rho \times l}$$  \hspace{1cm} (2)$$

Where $\rho$ is the apparent density that was determined by coating the wheat straw samples (prepared in the same way as the tensile strength specimen) with paraffin wax (with known density). The weight was measured both prior to and after the coating with paraffin wax. Volumetric pipettes and water were used to measure the volume of wax coated samples in a volumetric flask.

Strain energy per unit volume was calculated as the area below the stress-strain curve in the diagram with the percent of elongation as X-axis and stress as Y-axis. [19]

2.4. Hardgrove Grindability Index (HGI)

Determination of grindability was performed in a standard Hardgrove grinder (3200LB, AUBEMA, Germany) pursuant to the ASTM D409-51 (1961) standard. The test feed volume was 50 cm$^3$ with a particle size between 0.6 mm and 1.18 mm, this was done by pouring the particles into a 50 cm$^3$ volumetric flask and vigorously
Stamping on a wooden board to the point where further stamping did not reduce the volume of the material. The loading of the top grinding ring was 290 N and the grinding time was 3 min (377 radians of the mill at speed of 2.09 rad s\(^{-1}\)). The test sieve had a 75 µm mesh size and the Hardgrove Index was determined by Eq. (3) [20]:

\[
HGI = 13 + 6.93 \times m_H
\]  

Where \(m_H\) is the weight (in the units of gram) of the ground product passing the 75 µm sieve. The lower the number, the more difficult the material is to grind.

In addition to the wheat straw samples, a reference coal sample (RUKUZN, supplied by DONG Energy, Denmark) was tested. The sample was dried in an oven at 104 °C for 24 hours before the test, and the mass fraction of water was determined to be 9.0% on wet material basis (w.b.). HGI was measured for the original (wet), partially dried and totally dried coal sample according to ASTM standard test procedure as described in [20] by using the same fixed volume (50 cm\(^3\)) for each feed.

### 2.5. Heating value

A Bomb calorimeter (6300, Parr Instrument Company, USA) was used to determine the higher heating value (HHV). Initially, the calorimeter was calibrated using benzoic acid tablets. Torrefied wheat straw was milled in a cutting mill (SM2000, Retsch, Germany) and particles smaller than 0.6 mm were placed in the crucible and fired inside the bomb calorimeter using an ignition wire in the presence of oxygen. The measurements were repeated at least 2 times, and the average value was used for calculation. Ash content was determined by placing the samples in a muffle furnace at 550 °C for 3 hours, 2 measurements were taken for each condition. Sample crucibles were ashed and dried before the measurement, and the dry material content (\(DM\)% of each sample was determined by a moisture analyzer (Halogen moisture analyzer, Mettler Toledo, Switzerland). All data was calculated on dry and ash free basis (daf).

\[
AWL\% = 100 \times \left(1 - \frac{m_a}{m_p}\right)
\]  

\(AWL\%\)
\[ AWL\%_{(d)} = \frac{AWL\%}{100 - ash\%_{(r.b.)}} \times 100 \]  

(5)

\[ ash\%_{(r.b.)} = ash\%_{(r.b.)} \times \frac{100 - AWL\%}{100} \]  

(6)

\[ HHV_{(d)} = \frac{HHV}{100 - ash\%_{(r.b.)}} \times 100 \]  

(7)

\[ energy\ loss\%_{(d)} = \left[ 1 - \frac{HHV_{(d)}}{HHV_{104\degree C(d)}} \right] \times \left( 1 - \frac{AWL\%_{(d)}}{100} \right) \times 100 \]  

(8)

Where \( m_a \) and \( m_b \) stand for the sample mass after and before the torrefaction respectively. \( m_b \) was recorded right after the drying, making \( AWL\% \) already dry based. \( ash\%_{(r.b.)} \) denotes ash content in the raw material (untorrefied), whereas \( ash\%_{(t.b.)} \) is the ash content in the torrefied material. Both parameters are dry material based. Energy loss is defined as the total heating value loss of the same wheat straw samples after the torrefaction treatment. \( HHV_{104\degree C} \) means the heating value of oven dried (104 °C, 24 h) wheat straw.

### 2.6 Cell wall composition

The content of lignin, cellulose and hemicelluloses were determined for both untorrefied wheat straw and wheat straw torrefied at 300 °C for 2 hours according to ASTM E 1758-01 [21] and Kaar et al. [22]. Briefly, a representative sample that was smaller than 1mm was first made soluble in strong acid (72% H\textsubscript{2}SO\textsubscript{4}) at room temperature and then hydrolyzed in dilute acid (4% H\textsubscript{2}SO\textsubscript{4}) at 121 °C by autoclavation. Hemicelluloses and cellulose contents were determined by HPLC analysis of liberated sugar monomers. Klason lignin content was determined based on the filter cake, subtracting the ash content after incinerating the residues from the strong acid hydrolysis at 550 °C for 3 h.
3. Results and discussion

3.1. ATR-FT-IR

Figure 1: ATR-FTIR spectra of oven dried (104 °C) and torrefied wheat straw samples. All spectra are separated to ease the comparison.

Infrared spectra taken from wheat straw samples torrefied at different temperatures are shown in Figure 1 with the bands of interest being identified by their wavenumbers. The band at 670 cm\(^{-1}\) is characteristic for cellulose [23,24] and is an OH torsional vibration band. The fact that a significant decrease of this band is seen only for the highest temperatures between 270 °C and 300 °C shows that the cellulose component is largely stable until these temperatures are reached. The band at 1160 cm\(^{-1}\) is attributed to the antisymmetric stretching of C-O-C glycosidic linkages in both cellulose and hemicelluloses [25,26]. Its decrease is attributed to depolymerization and is most significant at the higher temperatures, and for 300 °C the band is practically absent. Gierlinger et al. attributed the band at 1240 cm\(^{-1}\) to the antisymmetric stretching of C-O-C of acetyl groups [26]. There are no acetyl groups existing in the hemicelluloses of wheat straw. However, for both reference xylans a band is found
at 1245 cm\(^{-1}\) and is of approximately the same strength as the (xylan) 900 cm\(^{-1}\) band. The assignment of the 1240 cm\(^{-1}\) band to lignin can also not be ruled out. The peak observed at 1505 cm\(^{-1}\) is diagnostic of lignin [25,27] and is placed in a spectral region devoid of polysaccharide peaks. No clear change of this peak is observed for most of the temperature range. However, at 300 °C it does appear to have diminished. The band at 1732 cm\(^{-1}\) is attributed to the carbonyl stretching band of carboxylic acid groups in hemicelluloses [26,27]. It starts to decrease from 250 °C, signifying a reduction in the amount of the carboxylic acid groups of hemicelluloses. This reduction is paralleled by the appearance of a new degradation product band at 1700 cm\(^{-1}\). When torrefaction temperature reaches 300 °C, the 1732 cm\(^{-1}\) band is completely eliminated, which suggests the complete removal of hemicelluloses. The narrow CH\(_2-\) stretching bands (superimposed a broader band) at approximately 2850 and 2920 cm\(^{-1}\) are ascribed to the aliphatic fractions of wax [27]. These bands for the C-H stretching can clearly be seen in spectra of extracted wax using hexane by work by Stelte, et al. [28]. These bands appear not to change significantly due to the heat treatment of torrefaction although a small decrease of these bands is suggested for the highest temperatures. It is possible that the higher molecular weight waxes may still be present in the samples torrefied at 300 °C, although further work needs to be done to confirm this.

By analyzing the FTIR spectra of the torrefied wheat straw samples, it can be concluded that there is no major structural change of the wheat straw samples torrefied below 200 °C. Increasing the temperature from 200 °C to 250 °C introduces distinct changes in the spectrum. These appear not to involve lignin or cellulose to any major extent, as the two characteristic bands of these components at 1505 and 670 cm\(^{-1}\) do not change. Thus degradation and depolymerization of hemicelluloses is proposed to account for the initial low temperature torrefaction effects. A higher temperature effect is most notable for the 270 °C to 300 °C transition and consists of the degradation of lignin and cellulose. The cell wall composition of both untorrefied wheat straw and wheat straw torrefied at 300 °C were determined, and the results (Table 1) support the findings from FTIR. At 300 °C torrefaction conditions, hemicelluloses are almost completely removed and cellulose is also reduced.
substantially. Furthermore, although some degradation of wax is indicated, its efficient removal by the heat
treatment during torrefaction has not been proved at the current operational conditions (300 °C, 2 hours).

Table 1: Mass fraction of hemicelluloses, cellulose and lignin in both raw and torrefied wheat straws (dry and ash free basis)

<table>
<thead>
<tr>
<th></th>
<th>Lignin</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wheat straw</td>
<td>21.28</td>
<td>35.64</td>
<td>27.78</td>
<td>84.70</td>
</tr>
<tr>
<td>Wheat straw-torrefied at 300°C for 2h</td>
<td>98.40</td>
<td>1.02</td>
<td>0.34</td>
<td>99.76</td>
</tr>
</tbody>
</table>

3.2. HGI

The reference coal sample at 3 different moisture contents on wet material basis (w.b.) (totally dried: 0%;
partially dried: 6.3%; wet: 9.0%) were first ground in the standard Hardgrove grinder, and HGI was determined
to be 33, 53, 68 respectively. Then the relationship between the mass fraction of the coal samples passing
through the 75 µm sieve after the grinding (x) and the equivalent HGI ($HGI_{equiv}$) was established in the similar
way as Bridgeman et al. [1]. The result is given in Eq. (9) with $R^2 = 0.9993$:

$$HGI_{equiv} = \frac{(x + 5.2521)}{0.3577} \quad (9)$$

This equation was then used to determine the equivalent HGI of the wheat straw samples torrefied at the
different temperatures. Meanwhile, standard HGI value was calculated according to Eq. (3). Both standard and
equivalent HGI are calculated and plotted in Figure 2. The standard HGI value of wet coal was measured to be
33, which is close to the value of wheat straw torrefied at 300 °C for 2 hours. It means that the mill can produce
similar amounts of fine particles by loading the same volume of the two materials. The HGI tests were repeated
for the wheat straw samples torrefied at 300 °C. It can be seen from the figure that there was no big improvement
of HGI when torrefaction temperature was lower than 200 °C and the HGI value increases sharply when
torrefaction temperature goes from 230 °C to 300 °C. FTIR spectra indicate that there is no major structural
change of samples torrefied below 200 °C, hemicelluloses start decomposition at 200 °C to 250 °C and are
removed totally when torrefaction temperature reaches 300 °C, while cellulose and lignin are found to start the
degradation at 270 °C to 300 °C. It can thus be concluded that the removal of hemicelluloses is the main reason of the increase of HGI, which means a better grindability.

Figure 2: HGI of oven dried (104 °C) and torrefied wheat straw

Furthermore, plots of weight percent of particles passing 75 µm and 250 µm after being ground in the Hardgrove ball mill are given in Figure 3. It can be seen that there is no big change before 200 °C. The largest increase in the fine particle fraction, which is smaller than 75 µm, happens in the range of 250 °C to 300 °C. For particles smaller than 250 µm it happens in the temperature range of 200 °C to 250 °C. The weight percent of reference coal particles at different moisture contents passing through 75 µm and 250 µm after grinding are 6.67% to 19.08%, and 31.26% to 41.95% respectively. This means that in order to produce similar grindability as coal, the torrefaction temperature should be at least 230 °C. At a torrefaction temperature of 260 °C, wheat straw sample has a similar equivalent HGI value as ‘totally dried coal’, but a higher percentage of particles passing through 250 µm sieve.
Figure 3: Mass fraction of particles passing through 75 µm, and 250 µm after grinding for oven dried and torrefied wheat straw.

In order to study the influence of residence time on the Hardgrove grindability, tests were also made for wheat straw torrefied at 250 °C for 0.5 h, 1 h, 2 h and 3 h respectively. Results are shown in Figure 4. It can be seen that for a torrefaction temperature of 250 °C, a 2-hour residence time is enough for improving the grindability of wheat straw samples.
3.3. Tensile strength

The results of the tensile strength measurements obtained by using both apparent density and caliper measurements are shown in Figure 5. From both methods, it can be seen that there is a clear decrease of breaking stress from 150 °C to 200 °C, and from 250 °C to 300 °C. Compared to the HGI results, both tests show a big improvement of grindability at a torrefaction temperature of 250 °C to 300 °C, and this finding is consistent with the FTIR analysis results discussed in 3.2. By comparing the mean strain energy (Figure 6), it can be concluded that wheat straw torrefied at 250 °C for 2 hours only requires about 1/5 to 1/7 of the energy, required to pull untreated, oven dried wheat straw apart.

The tensile strength of untreated wheat straw with mass fraction of water in the range of 8-65% on wet material basis (w.b.) found in the literature varies from 9 MPa to 38 MPa [18,29,30]. Contrary to these numbers, Kronbergs [31] reported a much higher value for wheat stalk, found to be (118.7±8.63) MPa. These data are
based on the wall area of the whole stalk sample at the failure cross-sections. Besides, Burmistrova [32] calculated stalk cross-section area based on the absolute dry weight of the wheat sample, the length of sample and the density of cellulose (1.55 g cm\(^{-3}\)). This physical cross-section area is smaller than the geometrical wall area by a factor of 5 to 10. Therefore the tensile strength, which was found to be in the range of 128 MPa to 399 MPa, is correspondingly larger than the results of the other quoted authors. Comparing the results obtained from oven dried wheat straw in this paper and the data mentioned above, it is found that the tensile strength is likely to be underestimated in most of the literature [18, 29, 30] where the whole stalk is used for the test. This is because the whole stalk does not break equally at the same time. In most cases, the weakest part breaks first while the other parts still hold together and only break when the force increases. Therefore, the cross section area of the whole stalk is bigger than the actual area where the break happens, leading to underestimated tensile strength.

Figure 5: Tensile strength of wheat straw dried in oven (104 °C, 24 h) and torrefied under different temperatures for 2 hours
Figure 6: Strain energy of same wheat straw as in Fig. 5 from both direct calliper measurement and indirect apparent density calculation.

3.4. Anhydrous weight loss and energy loss

The weight loss from the drying process (104 °C, 24 h) is quite constant, which is around 9-10% (w.b.). The weight loss in the torrefaction process can also be called anhydrous weight loss (AWL). The higher torrefaction temperature, the more mass is lost. When the temperature reaches 300 °C, around half of the material is lost.

Figure 7 shows the experimental and calculated results of ash content. The increase of experimental ash content is only due to the mass loss (non-ash part) from torrefaction. By comparing the calculated ash content, it can be concluded that torrefaction treatment below 300 °C and 2 hours has no influence on the ash content of wheat straw samples.

The higher heating value of wheat straw torrefied to different degrees (in form of \( AWL\% \)) on dry ash free basis is shown in Figure 8. Data obtained from different residence times at 250 °C are also presented in the plot (triangle markers). As shown, these points are located on the same trend line of HHV as a function of \( AWL\% \) obtained.
from different torrefaction temperatures with the same residence time (2 hours). This means that the parameter

\[ AWL\%_{\text{daf}} \]

can be used as a parameter to determine the effect of different torrefaction conditions, including
temperature and residence time, on the heating value of the biomass. This finding is in agreement with the study
done by Almeida et al. [33].

In addition, the influence of the degree of torrefaction as given by the \( AWL\% \) parameter on the energy loss is
also shown in Figure 8. When the torrefaction conditions get more severe, there is more anhydrous weight loss
and energy loss from the original material. The FTIR results show that hemicelluloses start the decomposition at
200-250 \(^{\circ}\)C and it lasts until 300 \(^{\circ}\)C, while cellulose and lignin start the decomposition at 270-300 \(^{\circ}\)C. So there is
more energy and mass loss at torrefaction temperatures ranging from 250 \(^{\circ}\)C to 300 \(^{\circ}\)C compared to from 200 \(^{\circ}\)C
to 250 \(^{\circ}\)C.

Furthermore, these two kinds of loss are not at the same ratio. Heating value is lost faster than the mass. The
energy loss at 300 \(^{\circ}\)C (33\%) is about 2.8 times of the energy loss at 250 \(^{\circ}\)C (12\%); while regarding anhydrous
weight loss this number is 2.3. So in order to preserve energy in the torrefied material, lower torrefaction
temperature and/or shorter residence time are preferred. On the other hand, if energy condensed material is
desired, it is better to have more severe torrefaction condition.
Figure 7: Ash content of wheat straw torrefied at different temperatures (denoted as ‘ash% (t.b.’), and calculated ash content of raw materials (denoted as ‘ash% (r.b.’). All data are on dry material basis.
Figure 8: Higher heating value and percent of energy loss of wheat straw torrefied at different degrees (150, 200, 220, 230, 250, 260, 270, 280, 290, 300 °C for 2 hours. ‘250C, 0.5-3 h’ represents the data collected at 250 °C torrefaction temperature with different residence time of 0.5, 1, 2, and 3 hours). All data are on dry and ash free basis.

4. Conclusion

By comparing the HGI of wheat straw samples torrefied at different temperatures, it can be seen that there is almost no improvement of the grindability for samples torrefied below 200 °C. In the torrefaction temperature range between 230 °C and 300 °C, the HGI value increases sharply. In the same range, tensile failure stress decreases from about 21-26 MPa to 4 MPa, which shows a close relation between the two properties. The FTIR analysis suggests that the removal of hemicelluloses, the degradation of which starts at 200-250 °C and finishes at about 300 °C, is the main reason for the improvement of grindability in this temperature range. Following grinding of the wheat straw torrefied at a temperature of 230 °C, the samples produce similar weight percentages of fine particles (<75 µm) as the tested wet coal sample (with 9.0% moisture content on wet basis), while similar percentages of fine particles as produced from ‘totally dried coal’ (with 0% moisture content) can be achieved at a torrefaction temperature of 260 °C.

However, tensile strength test was not proved to be more reproducible and repeatable than the HGI test. But on the other hand, strain energy measured from tensile failure strength suggests that about 80-85% of the energy can be saved when comparing torrefied wheat straw (250 °C, 2 h) with oven dried samples in the breaking process. Such numbers cannot be derived from HGI results.

By looking at the relationship between energy loss and weight loss, it is found that the percent of energy loss increases faster than the weight loss when torrefaction condition gets more severe and is probably because the degradation of lignin and cellulose happen at 270-300 °C. So in order to preserve energy in the torrefied material, lower torrefaction temperature and shorter residence time are preferred. On the other hand, if energy condensed material is desired, it is better to have more severe torrefaction condition.
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Reference


