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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

21 straw torrefied at different conditions was determined on a standard Hardgrove grinder. Both results showed an
22 improvement of grindability in the torrefaction temperature range 250-300 °C, which can be well explained by
23 the findings from FTIR analysis. At a torrefaction temperature of 260 °C and with a residence time of 2 hours,
24 wheat straw samples produced similar HGI values as coal (RUKUZN) with 0% moisture content. Under this
25 condition, the Anhydrous Weight Loss (AWL%) of the wheat straw sample was 30% on dry and ash free basis
26 (daf), and the higher heating value of the torrefied wheat straw was 24.2 MJ kg⁻¹ (daf). The energy loss
27 compared to the original material was 15% (daf).

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

29 **1. Introduction**

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

44 significantly better grinding properties and that further temperature increase had only minor effects. Further
45 studies about the torrefaction and grindability of wood samples have been made by [7-10].

46 Where these studies have shown the beneficial effect of torrefaction of woody biomass, grass samples such as
47 wheat straw present more difficulty. Wheat straw has some unique properties that differ from woody biomass.
48 The tenaciousness of the untreated wheat straw makes it almost impossible to grind in a ball mill, where the
49 tumbling action rather flattens the fibers instead of crushing and breaking them. This is related to the ultra
50 structural differences of the cell wall of wheat straw as compared to woody biomass. For example, wheat straw
51 fiber has a much thicker outer layer in the secondary cell wall based on volume percentage compared to spruce
52 tracheid. The fibrils in this layer are oriented laterally in cross helix making the defibrillation of grassy biomass
53 more difficult [11]. From a chemical point of view, there is also difference between wheat straw and woody
54 biomass. The main hemicelluloses found in hardwood are partially acetylated (4-O-methyl-D-
55 glucuronopyranosyl)-D-xylans, while hemicelluloses in wheat straw are more complex, mainly consisting of a
56 (1→4)-linked β -D-xylan with D-glucopyranosyluronic acid (or 4-O-methyl- α -D-glucopyranosyluronic acid)
57 groups attached at position 2, and L-arabinofuranosyl and D-xylopyranosyl groups attached at position 3. They
58 form hydrogen bonds with cellulose, covalent bonds (mainly α -benzyl ether linkages) with lignin, and ester
59 linkages with acetyl units and hydroxycinnamic acids. The cross-linking of hemicelluloses and lignin by
60 ferulates/diferulates in the wheat straw cell wall enhanced the difficulty of separating these two components [11].
61 Higher percentage of hemicelluloses in wheat straw compared with woody biomass also contributes to the better
62 linkage between the polymers.

63 In studies of heat-induced modifications of biomass properties, Svoboda et al. [12] summarized that the main
64 changes in biomass due to torrefaction involve decomposition of hemicelluloses and partial depolymerization of
65 lignin and cellulose. Bella et al. [13] heated American hardwoods to temperatures between 200 °C and 400 °C,
66 and found a lower cellulose and hemicelluloses resistance compared to lignin. Although some decomposition

67 temperatures for these compounds can be found in literature [5,8], there is a lack of experimental data indicating
68 the close relationship between the thermochemical and the grindability changes, especially for wheat straw.

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

77 The HGI was developed as a measure, which indicates how difficult it is to grind a specific coal to the particle
78 size necessary for effective combustion in a pulverized coal fired boiler [14]. In the standard method the HGI
79 value is based on the amount of sample passing through a 75 μm sieve after being ground in a standard
80 Hardgrove ball mill for 377 radians for each fixed amount of feed (50 g). Joshi [15] and Agus and Waters [16]
81 pointed out that the fixed mass approach is unsatisfactory for making direct comparisons among fuels with
82 densities differing a lot. To correct this situation and to bring evenness in grindability ratings of biomass and
83 coal, Bridgeman et al. [5] used the same fixed volume (50 cm^3) for each feed as opposed to a fixed mass (50 g).

84 As the HGI is based on an empirical method, it is not linked directly with any specific physical property of the
85 sample, and suffers from relative low reproducibility and repeatability. Therefore, as a supplement, it was
86 decided to investigate the tensile strength of the wheat straw samples before and after torrefaction. The tensile
87 strength is the maximum stress that a material can withstand while being pulled before breaking. Furthermore,
88 by measuring the elongation of the specimen while pulling it apart, it is possible to calculate the strain energy at
89 fracture per unit volume. Yigit [17] related the energy absorbed per unit new surface area created during

90 comminution and the strain energy per unit volume of a solid at fracture, and established mathematical models
91 assuming fracture by tensile stresses. Mathematical models of new surface area energy derived from different
92 fracture patterns all have a positive linear relationship with strain energy per unit volume, if the starting particle
93 size and the reduction ratio are constants. Although the models cannot fully represent the realistic fracture
94 pattern of a comminution process, they allow one to use the relative change of the strain energy at fracture under
95 tensile stress at different torrefaction temperatures as an indication of how much energy can be saved during
96 grinding under the same mill conditions.

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

103 **2. Material and methods**

104 **2.1. Torrefaction**

105 The wheat straw used in this study is from winter wheat (*Triticum aestivum* L.), which was the most grown
106 wheat species in Denmark in 2008. The straw was cut by hand in the field on the island of Funen, Denmark
107 (55°21'N 10°21'E) in August 2008, and stored indoors packed in the paper bags. Prior to the experiment, wheat
108 straw were selected and cut to about 30 cm long pieces. Samples were first dried in the oven at 104 °C for 24
109 hours, and then placed in an air tight metal container (15×31×10 cm) that could be heated in an oven
110 (Lyngbyovnen of type S 90, 3 × 380 V, 9 kW) to the desired torrefaction temperature. 0.5 dm³ min⁻¹ of nitrogen
111 was pumped through the sample container to create an inert atmosphere. The temperature of the oven was
112 measured in the centre of the chamber using thermocouples and this measurement was used for temperature

113 control. The residence time of the torrefaction process starts when the material temperature has reached the set
114 temperature until it starts to cool down. Torrefaction was carried out at 150, 200, 220, 230, 250, 260, 270, 280,
115 290 and 300 °C with residence time of 2 hours. Additional different residence times of 0.5, 1, 2, 3 hours were
116 tested at 250 °C.

117 **2.2. ATR-FTIR**

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

129 **2.3. Tensile strength**

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

134 Tensile tests of wheat straw torrefied at different temperatures were tested using a tensile tester (Vantage,
135 Thwing Albert, USA) with a video extensometer measuring the prolongation of the straw. The elongation rate

136 was 1mm min⁻¹ and stress was recorded using a 250 N load cell. Data from samples that failed close to the
137 aluminum tabs were rejected. Each measurement was repeated 4 times, except for wheat straw torrefied at 300
138 °C. Due to the brittleness of the sample, data were collected from only 2 samples. The tensile failure stress (or
139 ultimate tensile strength), σ , of the specimen was calculated from the Eq. (1) [18]:

$$140 \quad \sigma = \frac{F_t}{A} \quad (1)$$

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

$$146 \quad Area = \frac{m}{\rho \times l} \quad (2)$$

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

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

153 **2.4. Hardgrove Grindability Index (HGI)**

154 Determination of grindability was performed in a standard Hardgrove grinder (3200LB, AUBEMA, Germany)
155 pursuant to the ASTM D409-51 (1961) standard. The test feed volume was 50 cm³ with a particle size between
156 0.6 mm and 1.18 mm, this was done by pouring the particles into a 50 cm³ volumetric flask and vigorously

157 stamping on a wooden board to the point where further stamping did not reduce the volume of the material. The
158 loading of the top grinding ring was 290 N and the grinding time was 3 min (377 radians of the mill at speed of
159 2.09 rad s⁻¹). The test sieve had a 75 μm mesh size and the Hardgrove Index was determined by Eq. (3) [20]:

$$160 \quad HGI = 13 + 6.93 \times m_H \quad (3)$$

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

163 In addition to the wheat straw samples, a reference coal sample (RUKUZN, supplied by DONG Energy,
164 Denmark) was tested. The sample was dried in an oven at 104 °C for 24 hours before the test, and the mass
165 fraction of water was determined to be 9.0% on wet material basis (w.b.). HGI was measured for the original
166 (wet), partially dried and totally dried coal sample according to ASTM standard test procedure as described in
167 [20] by using the same fixed volume (50 cm³) for each feed.

168 **2.5. Heating value**

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

$$178 \quad AWL\% = 100 \times \left(1 - \frac{m_a}{m_b} \right) \quad (4)$$

179
$$AWL\%_{(daf)} = \frac{AWL\%}{100 - ash\%_{(r.b.)}} \times 100 \quad (5)$$

180
$$ash\%_{(r.b.)} = ash\%_{(t.b.)} \times \frac{100 - AWL\%}{100} \quad (6)$$

181
$$HHV_{(daf)} = \frac{HHV / DM\%}{100 - ash\%_{(t.b.)}} \times 100 \quad (7)$$

182
$$energyloss\%_{(daf)} = \left[1 - \frac{HHV_{(daf)}}{HHV_{104^{\circ}C(daf)}} \times \left(1 - \frac{AWL\%_{(daf)}}{100} \right) \right] \times 100 \quad (8)$$

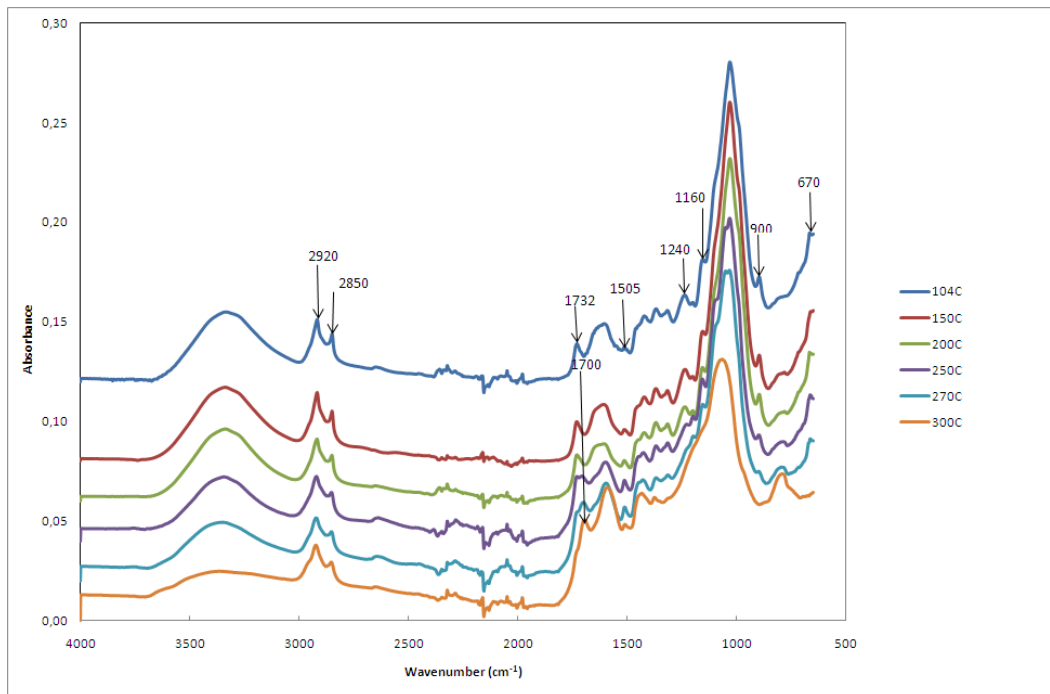
183 Where m_a and m_b stand for the sample mass after and before the torrefaction respectively. m_b was recorded right
 184 after the drying, making $AWL\%$ already dry based. $ash\%_{(r.b.)}$ denotes ash content in the raw material
 185 (untorrefied), whereas $ash\%_{(t.b.)}$ is the ash content in the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

188 **2.6 Cell wall composition**

189 The content of lignin, cellulose and hemicelluloses were determined for both untorrefied wheat straw and wheat
 190 straw torrefied at 300 °C for 2 hours according to ASTM E 1758-01 [21] and Kaar et al. [22]. Briefly, a
 191 representative sample that was smaller than 1mm was first made soluble in strong acid (72% H₂SO₄) at room
 192 temperature and then hydrolyzed in dilute acid (4% H₂SO₄) at 121 °C by autoclavation. Hemicelluloses and
 193 cellulose contents were determined by HPLC analysis of liberated sugar monomers. Klason lignin content was
 194 determined based on the filter cake, subtracting the ash content after incinerating the residues from the strong
 195 acid hydrolysis at 550 °C for 3 h.

196 3. Results and discussion

197 3.1. ATR-FT-IR



198

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

201 Infrared spectra taken from wheat straw samples torrefied at different temperatures are shown in Figure 1 with
202 the bands of interest being identified by their wavenumbers. The band at 670 cm^{-1} is characteristic for cellulose
203 [23,24] and is an OH torsional vibration band. The fact that a significant decrease of this band is seen only for
204 the highest temperatures between 270 °C and 300 °C shows that the cellulose component is largely stable until
205 these temperatures are reached. The band at 1160 cm^{-1} is attributed to the antisymmetric stretching of C-O-C
206 glycosidic linkages in both cellulose and hemicelluloses [25,26]. Its decrease is attributed to depolymerization
207 and is most significant at the higher temperatures, and for 300 °C the band is practically absent. Gierlinger et al.
208 attributed the band at 1240 cm^{-1} to the antisymmetric stretching of C-O-C of acetyl groups [26]. There are no
209 acetyl groups existing in the hemicelluloses of wheat straw. However, for both reference xylans a band is found

210 at 1245 cm^{-1} and is of approximately the same strength as the (xylan) 900 cm^{-1} band. The assignment of the 1240
211 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
212 is placed in a spectral region devoid of polysaccharide peaks. No clear change of this peak is observed for most
213 of the temperature range. However, at $300\text{ }^{\circ}\text{C}$ it does appear to have diminished. The band at 1732 cm^{-1} is
214 attributed to the carbonyl stretching band of carboxylic acid groups in hemicelluloses [26,27]. It starts to
215 decrease from $250\text{ }^{\circ}\text{C}$, signifying a reduction in the amount of the carboxylic acid groups of hemicelluloses. This
216 reduction is paralleled by the appearance of a new degradation product band at 1700 cm^{-1} . When torrefaction
217 temperature reaches $300\text{ }^{\circ}\text{C}$, the 1732 cm^{-1} band is completely eliminated, which suggests the complete removal
218 of hemicelluloses. The narrow CH_2 - stretching bands (superimposed a broader band) at approximately 2850 and
219 2920 cm^{-1} are ascribed to the aliphatic fractions of wax [27]. These bands for the C-H stretching can clearly be
220 seen in spectra of extracted wax using hexane by work by Stelte, et al. [28]. These bands appear not to change
221 significantly due to the heat treatment of torrefaction although a small decrease of these bands is suggested for
222 the highest temperatures. It is possible that the higher molecular weight waxes may still be present in the
223 samples torrefied at $300\text{ }^{\circ}\text{C}$, although further work needs to be done to confirm this.

224 By analyzing the FTIR spectra of the torrefied wheat straw samples, it can be concluded that there is no major
225 structural change of the wheat straw samples torrefied below $200\text{ }^{\circ}\text{C}$. Increasing the temperature from $200\text{ }^{\circ}\text{C}$ to
226 $250\text{ }^{\circ}\text{C}$ introduces distinct changes in the spectrum. These appear not to involve lignin or cellulose to any major
227 extent, as the two characteristic bands of these components at 1505 and 670 cm^{-1} do not change. Thus
228 degradation and depolymerization of hemicelluloses is proposed to account for the initial low temperature
229 torrefication effects. A higher temperature effect is most notable for the $270\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ transition and consists
230 of the degradation of lignin and cellulose. The cell wall composition of both untorrefied wheat straw and wheat
231 straw torrefied at $300\text{ }^{\circ}\text{C}$ were determined, and the results (Table 1) support the findings from FTIR. At $300\text{ }^{\circ}\text{C}$
232 torrefaction conditions, hemicelluloses are almost completely removed and cellulose is also reduced

233 substantially. Furthermore, although some degradation of wax is indicated, its efficient removal by the heat
 234 treatment during torrefaction has not been proved at the current operational conditions (300 °C, 2 hours).

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

	Lignin	Cellulose	Hemicellulose	Total
Raw wheat straw	21.28	35.64	27.78	84.70
Wheat straw-torrefied at 300 °C for 2h	98.40	1.02	0.34	99.76

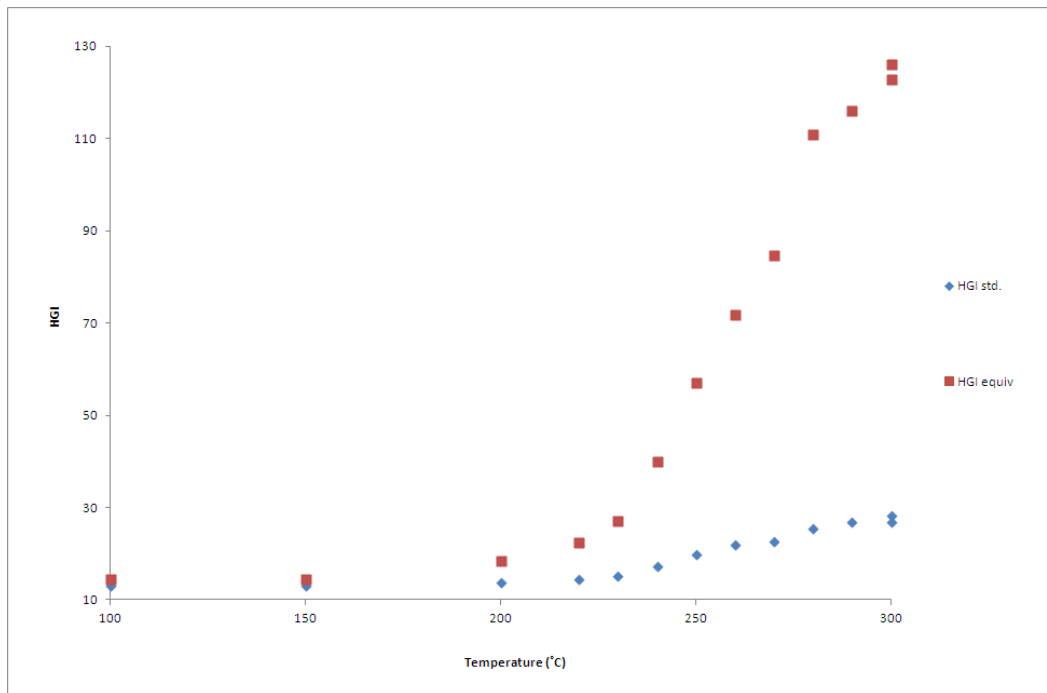
236 **3.2. HGI**

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

242
$$HGI_{equiv} = \frac{(x + 5.2521)}{0.3577} \quad (9)$$

243 This equation was then used to determine the equivalent HGI of the wheat straw samples torrefied at the
 244 different temperatures. Meanwhile, standard HGI value was calculated according to Eq. (3). Both standard and
 245 equivalent HGI are calculated and plotted in Figure 2. The standard HGI value of wet coal was measured to be
 246 33, which is close to the value of wheat straw torrefied at 300 °C for 2 hours. It means that the mill can produce
 247 similar amounts of fine particles by loading the same volume of the two materials. The HGI tests were repeated
 248 for the wheat straw samples torrefied at 300 °C. It can be seen from the figure that there was no big improvement
 249 of HGI when torrefaction temperature was lower than 200 °C and the HGI value increases sharply when
 250 torrefaction temperature goes from 230 °C to 300 °C. FTIR spectra indicate that there is no major structural
 251 change of samples torrefied below 200 °C, hemicelluloses start decomposition at 200 °C to 250 °C and are
 252 removed totally when torrefaction temperature reaches 300 °C, while cellulose and lignin are found to start the

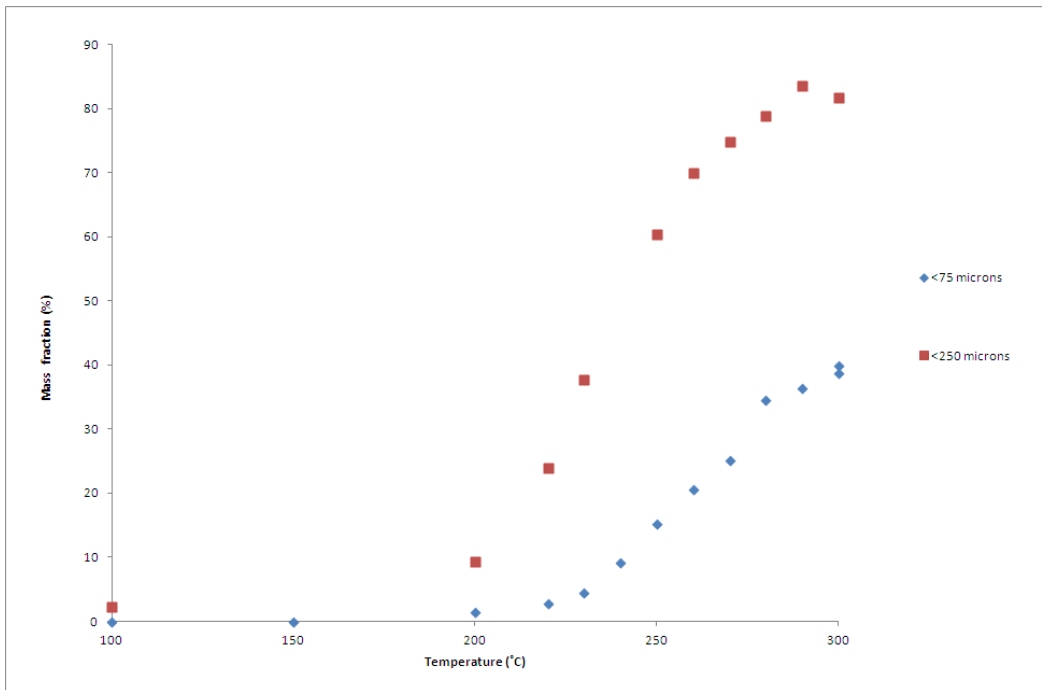
253 degradation at 270 °C to 300 °C. It can thus be concluded that the removal of hemicelluloses is the main reason
254 of the increase of HGI, which means a better grindability.



255

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

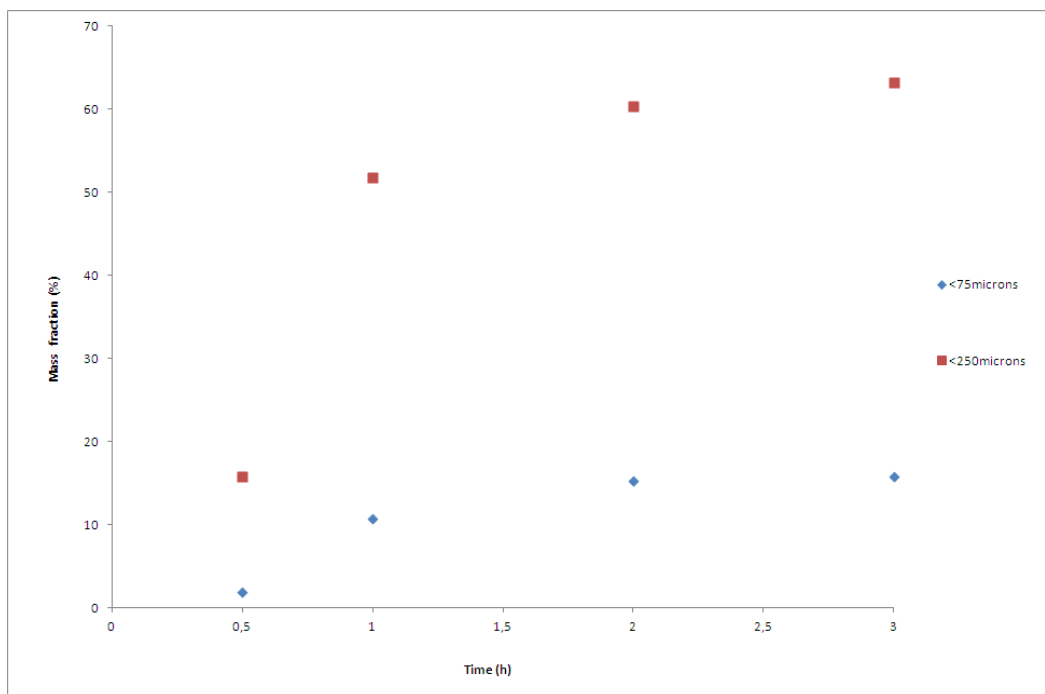
257 Furthermore, plots of weight percent of particles passing 75 µm and 250 µm after being ground in the Hardgrove
258 ball mill are given in Figure 3. It can be seen that there is no big change before 200 °C. The largest increase in
259 the fine particle fraction, which is smaller than 75 µm, happens in the range of 250 °C to 300 °C. For particles
260 smaller than 250 µm it happens in the temperature range of 200 °C to 250 °C. The weight percent of reference
261 coal particles at different moisture contents passing through 75 µm and 250 µm after grinding are 6.67% to
262 19.08%, and 31.26% to 41.95% respectively. This means that in order to produce similar grindability as coal, the
263 torrefaction temperature should be at least 230 °C. At a torrefaction temperature of 260 °C, wheat straw sample
264 has a similar equivalent HGI value as ‘totally dried coal’, but a higher percentage of particles passing through
265 250 µm sieve.



266

267 **Figure 3: Mass fraction of particles passing through 75 μm , and 250 μm after grinding for oven dried and torrefied wheat straw.**

268 In order to study the influence of residence time on the Hardgrove grindability, tests were also made for wheat
 269 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
 270 that for a torrefaction temperature of 250 °C, a 2-hour residence time is enough for improving the grindability of
 271 wheat straw samples.



272

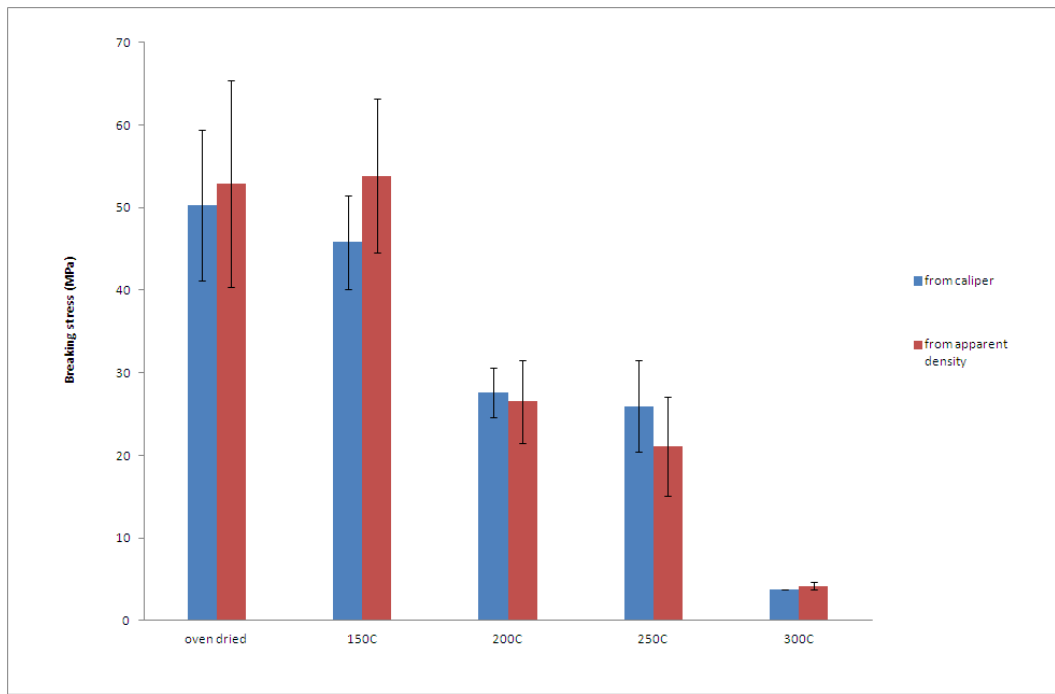
273 **Figure 4: Mass fraction of particles passing 75 μm , and 250 μm after grinding for wheat straw torrefied at 250 $^{\circ}\text{C}$ for difference**
 274 **time.**

275 3.3. Tensile strength

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

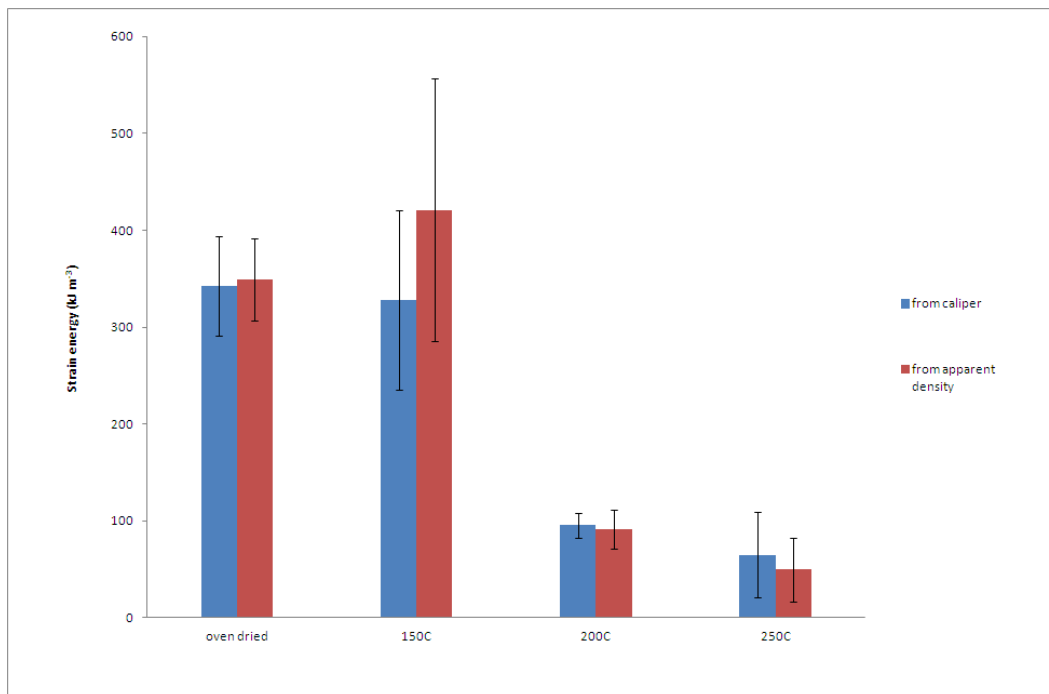
283 The tensile strength of untreated wheat straw with mass fraction of water in the range of 8-65% on wet material
 284 basis (w.b.) found in the literature varies from 9 MPa to 38 MPa [18,29,30]. Contrary to these numbers,
 285 Kronbergs [31] reported a much higher value for wheat stalk, found to be (118.7 \pm 8.63) MPa. These data are

286 based on the wall area of the whole stalk sample at the failure cross-sections. Besides, Burmistrova [32]
287 calculated stalk cross-section area based on the absolute dry weight of the wheat sample, the length of sample
288 and the density of cellulose (1.55 g cm^{-3}). This physical cross-section area is smaller than the geometrical wall
289 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
290 MPa, is correspondingly larger than the results of the other quoted authors. Comparing the results obtained from
291 oven dried wheat straw in this paper and the data mentioned above, it is found that the tensile strength is likely to
292 be underestimated in most of the literature [18,29,30] where the whole stalk is used for the test. This is because
293 the whole stalk does not break equally at the same time. In most cases, the weakest part breaks first while the
294 other parts still hold together and only break when the force increases. Therefore, the cross section area of the
295 whole stalk is bigger than the actual area where the break happens, leading to underestimated tensile strength.



296

297 **Figure 5: Tensile strength of wheat straw dried in oven (104 °C, 24 h) and torrefied under different temperatures for 2 hours**



298

299 **Figure 6: Strain energy of same wheat straw as in Fig.5 from both direct calliper measurement and indirect apparent density**
 300 **calculation**

301 **3.4. Anhydrous weight loss and energy loss**

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

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

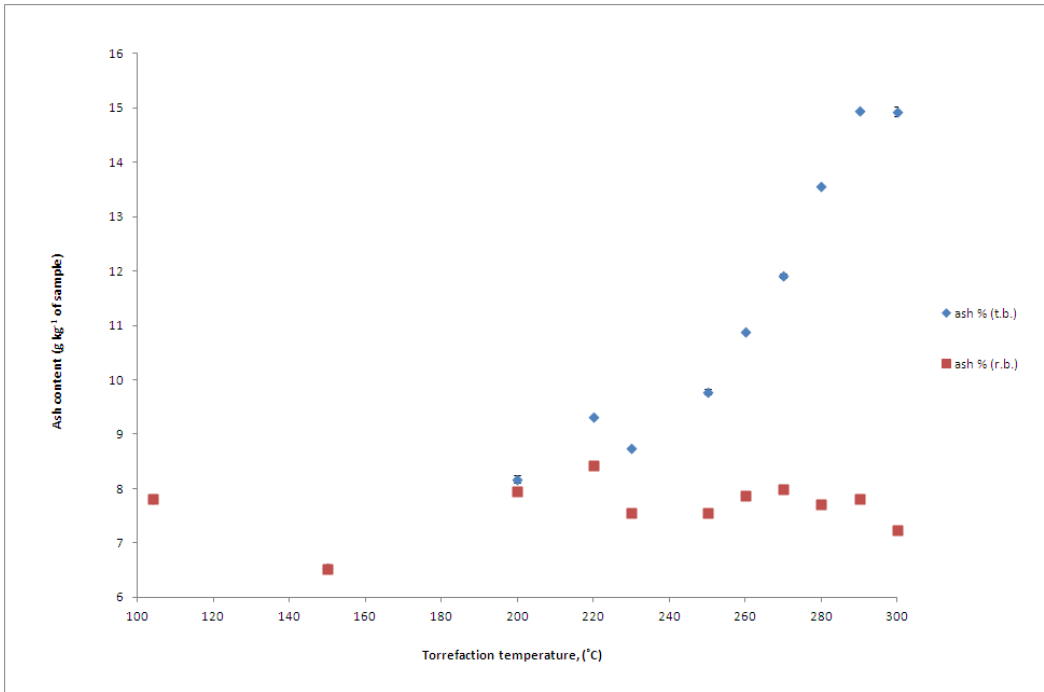
309 The higher heating value of wheat straw torrefied to different degrees (in form of *AWL%*) on dry ash free basis is
 310 shown in Figure 8. Data obtained from different residence times at 250 °C are also presented in the plot (triangle
 311 markers). As shown, these points are located on the same trend line of HHV as a function of *AWL%* obtained

312 from different torrefaction temperatures with the same residence time (2 hours). This means that the parameter
313 $AWL\%_{(daf)}$ can be used as a parameter to determine the effect of different torrefaction conditions, including
314 temperature and residence time, on the heating value of the biomass. This finding is in agreement with the study
315 done by Almeida et al. [33].

316 In addition, the influence of the degree of torrefaction as given by the $AWL\%$ parameter on the energy loss is
317 also shown in Figure 8. When the torrefaction conditions get more severe, there is more anhydrous weight loss
318 and energy loss from the original material. The FTIR results show that hemicelluloses start the decomposition at
319 200-250 °C and it lasts until 300 °C, while cellulose and lignin start the decomposition at 270-300 °C. So there is
320 more energy and mass loss at torrefaction temperatures ranging from 250 °C to 300 °C compared to from 200 °C
321 to 250 °C.

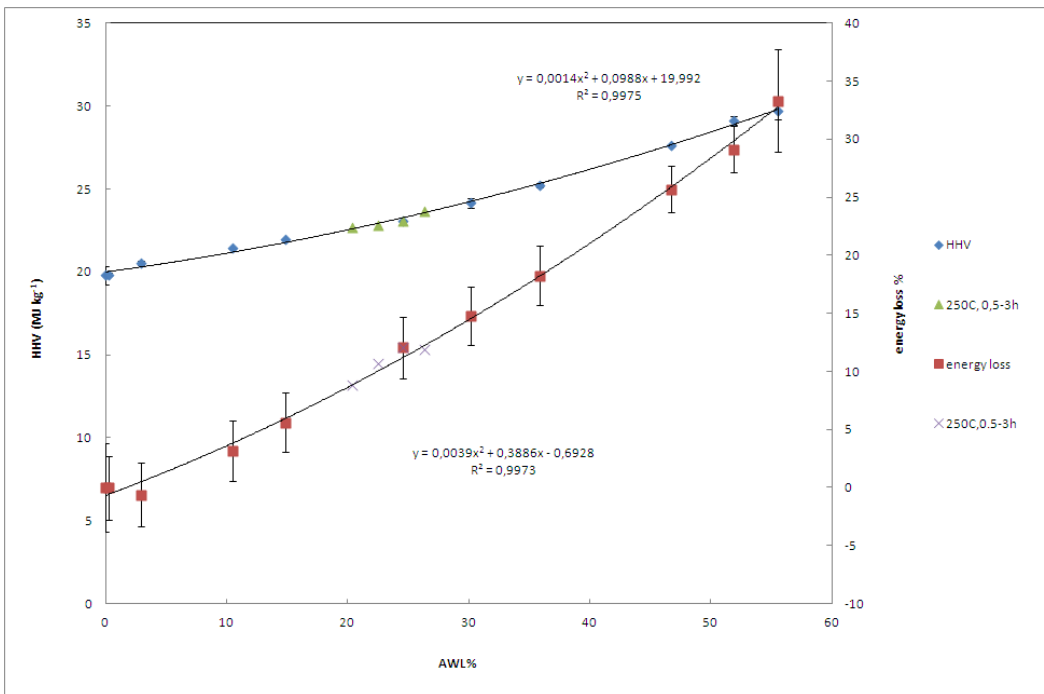
322 Furthermore, these two kinds of loss are not at the same ratio. Heating value is lost faster than the mass. The
323 energy loss at 300 °C (33%) is about 2.8 times of the energy loss at 250 °C (12%); while regarding anhydrous
324 weight loss this number is 2.3. So in order to preserve energy in the torrefied material, lower torrefaction
325 temperature and/or shorter residence time are preferred. On the other hand, if energy condensed material is
326 desired, it is better to have more severe torrefaction condition.

327



328 **Figure 7: Ash content of wheat straw torrefied at different temperatures (denoted as ‘ash% (t.b.)’), and calculated ash content of**
329 **raw materials (denoted as ‘ash% (r.b.)’). All data are on dry material basis.**

330



331 **Figure 8: Higher heating value and percent of energy loss of wheat straw torrefied at different degrees (150, 200, 220, 230, 250,**
332 **260, 270, 280, 290, 300 °C for 2 hours. '250C, 0.5-3 h' represents the data collected at 250 °C torrefaction temperature with**
333 **different residence time of 0.5, 1, 2, and 3 hours). All data are on dry and ash free basis.**

334 **4. Conclusion**

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

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

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

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