INVESTIGATION OF REGULARITIES OF PELLETIZED BIOMASS THERMAL DEFORMATIONS DURING PYROLYSIS

by

Rolandas PAULAUSKAS**[*]*, Nerijus STRIUGAS, Kestutis ZAKARAUSKAS, Algis DZIUGYS, and Lina VOROTINSKIENE***

Laboratory of Combustion Processes, Lithuanian Energy Institute, Kaunas, Lithuania

Original scientific paper
https://doi.org/10.2298/TSCI160916090P

Gasification process is a fairly complicated matter and using pelletized biomass for the gasification mostly results in fuel agglomeration. The pelletized biomass moving from the pyrolysis zone to the oxidation zone sticks together in lumps and disrupts entire process. In order to determine the regularities of thermal deformations, experimental research of pelletized biomass thermal deformations during pyrolysis were performed in a horizontal pyrolysis reactor from 300-900 °C temperature capturing wood particle, wheat straw and wood pellet radial changes by a digital camera. Also the center temperature and the mass loss of samples were measured to determine cause of biomass thermal deformations. Observed results reveal that when increasing the pyrolysis temperature from 400-900 °C, the wheat straw and wood pellets expand at the beginning of pyrolysis process and after it start to shrink, while wood particle is only affected by shrinkage. The swelling effect of pelletized samples starts decreasing over 600-650 °C heating temperature and disappears when the temperature is higher than 850 °C. Biomass shrinkage intensifies exponentially as the heating temperature increases till 700-750 °C. However, the final shrinkage starts to decrease as the heating temperature increases from 700-750 to 900 °C due to swelling of formed char.

Determined phenomenon of pelletized biomass swelling explains cause of fuel adhesion in pyrolysis zone of gasifier. Besides estimated regularities of biomass thermal deformations upon pyrolysis could be used to improve the existing numerical models of biomass pyrolysis.

Key words: *pelletized biomass, pyrolysis, swelling, shrinkage*

Introduction

Tightening requirements on environmental protection result in increasing usage of renewable fuel resources [1] for electricity and heat production due to low CO_2 emissions. In addition, it aims to use not only the high-quality biomass, but low-quality as well. One of the options to produce heat or electricity from lower quality biomass is to use pelletized low-quality biomass for gasification whereby solid fuel is converted into valuable producer gas. However, the biomass gasification process, where gas production mainly consists of pyrolysis (devolitilization) and char conversion stage, is a fairly complicated matter and use of pelletized biofuel for the gasification mostly results in fuel agglomeration due to the expansion of pellets and stops the entire process.

[*] Corresponding author, e-mail: rolandas.paulauskas@lei.lt

Biomass is a complex substance due to its structure, porosity, mixed composition and different physical properties in the longitudinal, tangential, and radial directions. When biomass is inserted into a pyrolysis reactor, a number of chemical and physical processes take place: dehydration, preheating, devolitilization, and charring. Due to these processes, thermal conversion of biomass occurs resulting in shrinkage of the pellets. According to [2], shrinkage of biomass is related to processes on microscopic and molecular level such as cracks, scission of polymer chains due to influence of heating rate. Mostly shrinking of wood particle has been investigated for a few decades. Volumetric shrinking upon pyrolysis was studied for different types of wood and temperatures and it was found that a birch particle shrinks 80% of its original size at 700 °C [3], a cubic wood particle – from 45-70% , respectively, at 350-900 °C [4]. Radial shrinkage of a spherical wood particle was examined by Huang *et al*., [5] pyrolyzing a sample from 400-700 °C and the results showed decrease of a wood sphere from 84.6-74% of the original size. Investigations of wood particle shrinkage in three directions were expanded by performing experiments upon pyrolysis, combustion, and gasification processes: Japanese Cyprus wood cylinders shrink about 70% and 80% in longitudinal direction and about 60% and 20% in axial direction, respectively, at 1 C/s and 30 C/s heating rate during pyrolysis [6], while at carbonization process [2] cubic tulip poplar particles shrinks from 10-21% in axial direction, from 20-32% in radial direction, and from 33-41% in tangential direction at 400-1600 °C temperature. At higher carbonization temperature (1600-2500 °C) tangential shrinkage increases from 42-44%, radial from 32-33%, and axial shrinkage decreases from 21-19%. The obtained results of Casuarina wood particle shrinking from combustion process in the temperature range of 650-850 °C [7] showed that increasing the sample length from 8-20 mm decreased the longitudinal shrinkage from 17-11%, and the transverse shrinkage also decreased with the increase in the initial sample diameter: transverse shrinkage from 28.6-14% with l/d ratio decreased from 10-0.2.

Pelletized fuel changes during thermal conversion are not so well investigated and only a few works [8, 9] concentrate on it. Only swelling and shrinking of the recovered solid waste (RDF) pellets and wheat straw pellet were researched during pyrolysis by Swedish scientists [9]. Results revealed that the RDF pellets expand by 54% and 58% of the initial volume at 550 °C and 660 °C heating temperature, respectively, and samples shrank only to the initial volume. The tendency of the straw pellet swelling and shrinking was different: first, the pellet expanded to 18% of the initial volume at 660 °C heating temperature and after that began to shrink to 44% of the initial volume [9]. According to the authors [9], swelling effect of RDF pellets may occur due to eruption of volatiles when melted groups of plastic forms an unstable liquid layer over the surface complicating volatile emission from deeper layers. However, composition of RDF pellets differs from that of the biomass pellets and ongoing processes which influence the swelling of RDF pellets could not be related to expansion of pelletized biomass. Also the measured swelling values of RDF pellets are obtained in a narrow range of heating temperatures and do not show a tendency of swelling with growing heating temperature.

In order to determine the regularities of pelletized biomass shrinking and swelling and develop mathematical formulas of biomass thermal deformations investigation of a cylindrical wood particle, a wood pellet and a wheat straw pellet the thermal conversion were performed in a preheated pyrolysis reactor at a constant temperature from 300-900 °C capturing size changes by a video camera and measuring mass loss.

Material characterization

Wood pellets (produced from birch sawdust), wheat straw pellets and cylindrical wood particles (produced from birch) were used for experimental research and the diameter of all samples was 8 ± 0.5 mm, the length was 18 ± 1.5 mm. Before investigation of biomass thermal deformations, the ultimate, proximate, and biochemical analyses of samples were acquired. The ultimate and proximate analysis were performed using an IKA C5000 calorimeter, a Flash 2000 CHNS analyzer in accordance with: LST EN 14774-1 (moisture content), LST EN 14918 (HHV), LST EN 14775 (ash content), LST EN 15148 (volatile content), and LST EN 15104 (CHNS content). Biochemical composition of samples was obtained by NDF and ADF analyzes using the ANKOM procedure with a polyester bag and the method of Van Soest. The obtained characteristics are shown in tab. 1.

Table 1. Characteristics of biomass samples

Parameter	Wood pellets	Wheat straw pellets	Cylindrical wood particle
Ultimate analysis, [wt.%] (dry basis)			
Carbon	51.22	45.84	49.59
Hydrogen	5.56	5.16	5.36
Oxygen (diff.)	43.20	47.67	45.03
Nitrogen	0.01	1.12	0.01
Sulphur	0.01	0.21	0.01
Proximate analysis			
Moisture content, [%]	6.68	8.28	5.83
Ash, [%]	0.7	4.9	0.2
HHV, [MJkg^{-1}]	18.77	16.57	17.49
LHV, [MJkg^{-1}]	17.47	15.33	16.25
Biochemical analysis, [wt.%]			
Hemicellulose	14.2	29.9	19.6
Cellulose	51.7	43.5	61.3
Lignin	25.4	6.22	14.4

Research methodology

In order to determine the regularities of pelletized biomass shrinking and swelling, two separate investigations were performed. First, biomass thermal deformations were researched at 300-900 °C heating temperature using the electrically heated horizontal tubular furnace Nabertherm RS 80/500/13 where an inert environment was created by a controlled nitrogen flow, fig. 1. A special pad with the sample, where a K-type thermocouple was installed to measure the center temperature of the sample, was placed in the heating tube and the thermal deformation of biomass samples during pyrolysis were captured by digital camera Fuji HS25 EXR, fig. 1. The experiments were performed at a constant heating temperature ranging from 300-900 °C in 50°C increments. The high-resolution (1920 × 1080 pixels) recorded videos of sample changes were analyzed using GIMP software, where each 145th captured video frame was converted into a photo and the sample diameter was measured with a digital ruler in pixels with 1 pixel accuracy. The biomass sample diameter of 8 mm matched to 210 ±1 pixels at the initial time of the pyrolysis process. The measured diameter in pixels was expressed as the relative units.

Second, mass loss of the samples during pyrolysis was studied using the same electrically heated horizontal tubular furnace, fig. 2. The furnace was assembled vertically and a heat-

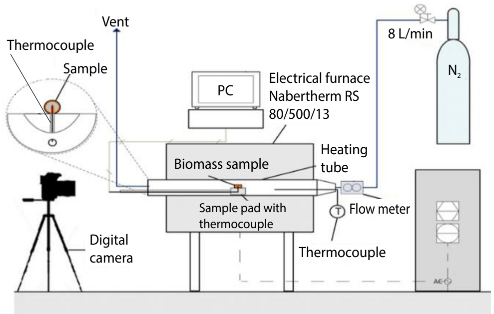

Figure 1. Experimental rig for determination of radial changes of a biomass sample

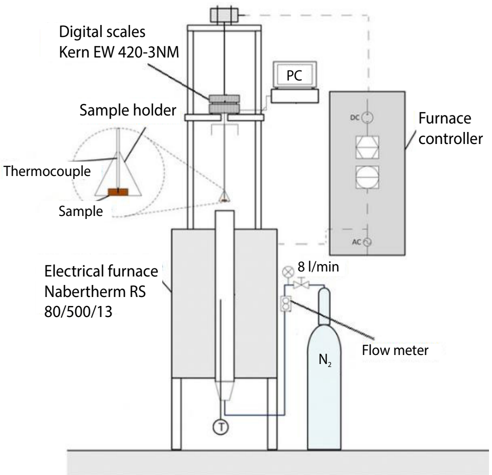

Figure 2. Experimental scheme of mass loss determination of biomass sample

ing tube was mounted inside the furnace. One end of the working tube was supplied with a nitrogen-flow, the other end of the tube was left open for placing a bracket holding the sample.

A special frame with a moving tray was mounted on the top of furnace and a digital scale Kern MSV was placed on the tray. A special rod with a bracket of stainless steel mesh holding a K-type thermocouple installed inside to measure the center temperature of the sample, was attached to the measurement point at the scale bottom. One additional thermocouple was installed in the working tube and used to measure the heating temperature affected by the nitrogen flow. Nitrogen-flow of 8 L/min, controlled by the flow meter was maintained into the furnace when the heating temperature reached the desired level. From this point, the sample was placed in the bracket, fed into the heating tube through the open end and measurements started. The mass loss data from the scale was collected using software Kern BC2006 and the center temperature values were collected by the data logger PICO and all the data sent to the computer. When mass changes of the sample was observed no more, the bracket with the sample was extracted from the heating tube and left to cool down. Measurements were repeated three times in the heating temperature range of 300-900 °C in 50 °C increments.

Size changes and mass loss of biomass samples during pyrolysis

Obtained data from the experiments were compared and analyzed, and diameter changes *vs*. mass loss at 300, 400, 650, and 850 °C from both experiments are presented in this chapter.

At low heating temperature (300 °C) only water evaporation and neglible decomposition of biomass samples take place causing a barely noticeable final shrinkage: the wood particle, the wood pellet, and the wheat straw pellet shrink by 2.1%, 1.2%, and 5.4% of the initial diameter, respectively. During the dehydration stage, which lasts until the center temperature, T_C, of samples reaches 125 °C, see fig. 3, the wood particle, the wood pellet, and the wheat straw pellet lose 3.7%, 2.3%, and 0.4% of the initial mass. From this point, decomposition of hemicellulose intensifies leading to increase of mass loss, see fig. 3, where the residual mass of the wood particle, the wood pellet, and the wheat straw pellet are 79%, 86%, and 84% at the end of the experiment, fig. 3.

At higher (400 °C) heating temperature, dehydration process shifts towards the higher temperature up to 130 °C and, after the water evaporation is completed, decomposition of

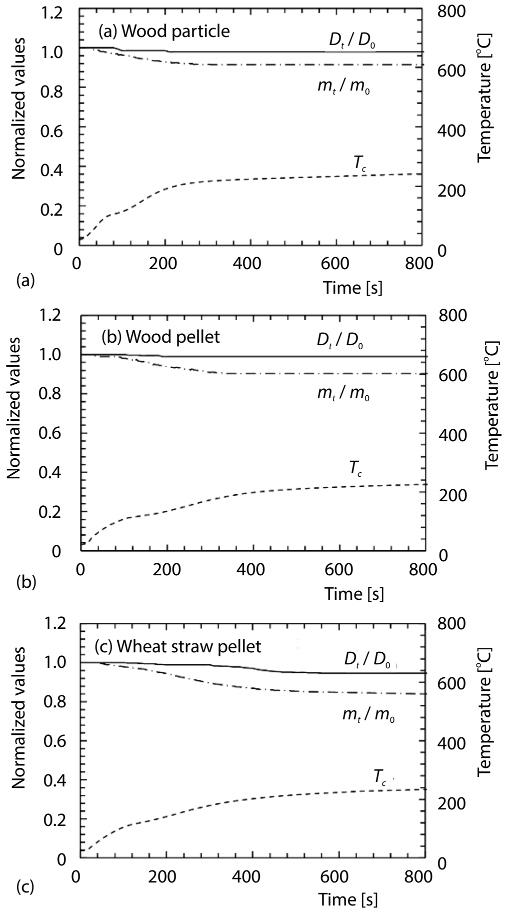

Figure 3. Size changes and mass loss of biomass samples *vs.* time during pyrolysis at 300 °C heating temperature

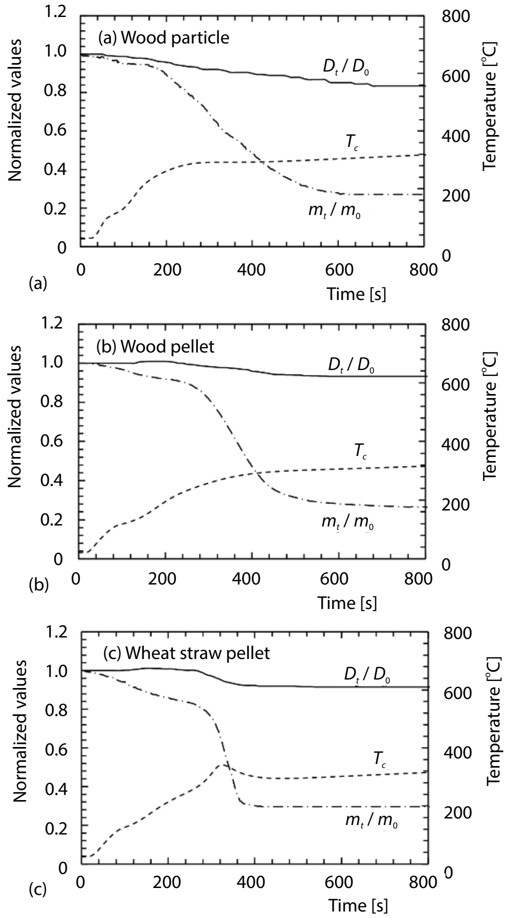

Figure 4. Size changes and mass loss of biomass samples *vs.* time during pyrolysis at 400 °C heating temperature

hemicellulose, lignin and cellulose begins. As it can be seen from fig. 4, biomass samples stop to shrink when mass loss stabilizes, *i. e.*, volatile emission has ended. Profiles of the center temperature imply that a wood particle overheats faster than pelletized samples and only shrinkage of the particle is observed, see T_C in fig. 4. Particle shrinks to 82.5% of its initial diameter losing 74% of its initial mass.

Meanwhile, at the end of dehydration process pelletized biomass is affected by negligible swelling phenomenon – diameter of pellets expands about 1%, fig. 4. With the beginning of hemicellulose decomposition, expanded pellets start to shrink and, in the end of thermal conversion, the residual diameter is 93.2% and 91.4% for wood and straw pellets, respectively, with mass loss of 74% and 72% of the initial mass.

With growing heating temperature (650 °C), thermal conversion of samples is more intensive, water evaporation process shifts towards higher center temperatures of up to 150 °C for all the samples, fig. 5. Wood particle is affected by fast thermal conversion (80% of mass in 200 seconds) resulting in shrinkage to 34.3% of the initial diameter. At this temperature point,

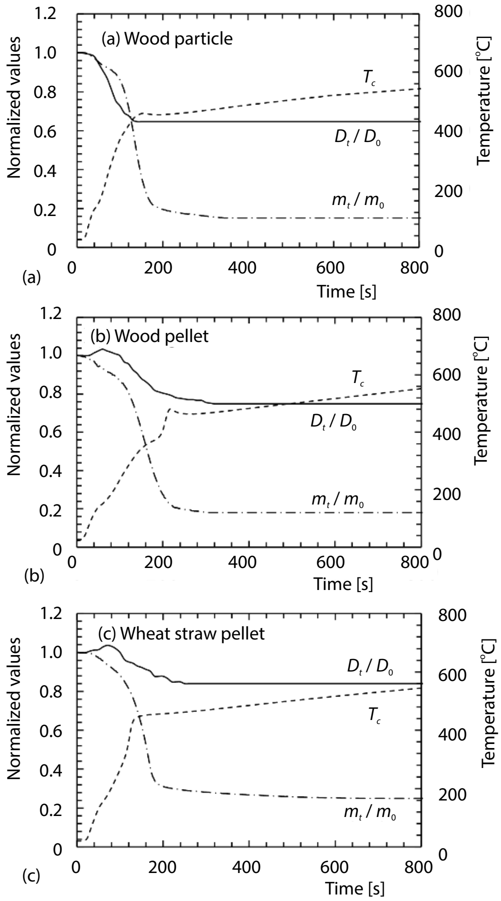

Figure 5. Size changes and mass loss of biomass samples *vs*. time during pyrolysis at 650 °C heating temperature

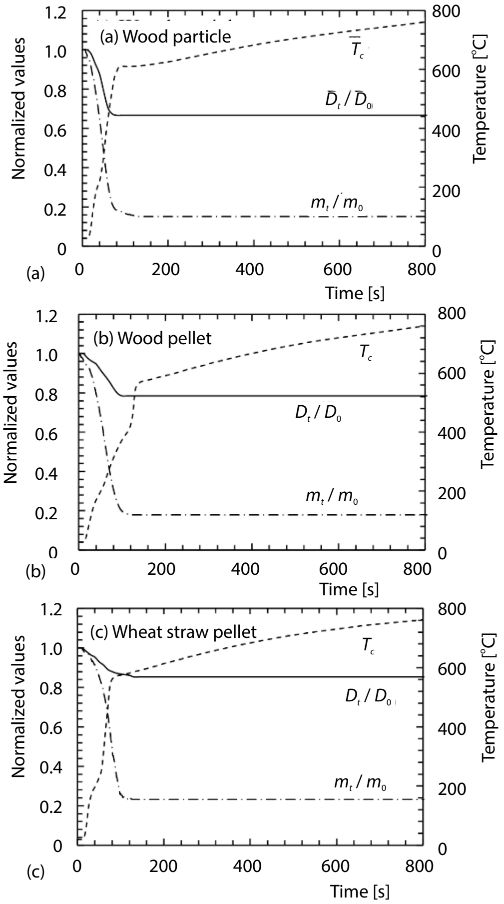

Figure 6. Size changes and mass loss of biomass samples *vs*. time during pyrolysis at 850 °C heating temperature

swelling effect of pelletized samples takes place earlier (after 30 seconds from the beginning of the experiment) and is most intensive: a wheat straw pellet and a wood pellet expand by 3.4% and 4.2% of the initial diameter, respectively, fig. 5. Pelletized samples start to shrink after dehydration process ends and devolitilization starts (the T_C, is over 150°C with 5% mass loss) and the wood pellet diameter decreases linearly to 75.6% of the initial diameter, and the wheat straw pellet diameter – to 85.8% of the initial diameter, losing 82% and 75% of mass, respectively, fig. 5.

Swelling effect of pelletized samples is no more observed at 850 °C heating temperature and only shrinkage dominates for all the samples, fig. 6. The thermal conversion of wood particle is most intensive (85% of mass in 100 seconds) and the particle starts to shrink immediately after placing it into the heated tube: it shrinks to 66% of the initial diameter. Thermal conversion of pelletized samples are identical for each particle type (it ends after 120 seconds with 83% and 77% mass loss for the wood pellet and the wheat straw pellet, respectively) and is 1.2 times slower than for the wood particle. The measured shrinkage values are 21.6% for the wood pellet and 14.6% of the initial diameter for the wheat straw pellet, fig. 6.

Regularities of thermal deformations of biomass

Final swelling and shrinking values and residual mass of biomass samples increasing heating temperature are presented graphically in fig. 7. Expansion of wood pellet depends on heating temperature and maximum values in range of 1.2-3.9% are proportional to heating temperature from 400-600 °C. With growing heating temperature over 600 °C swelling effect linearly diminishes and over 850 °C heating temperature it disappears. However, the tendency of wheat straw pellet expansion is different from that determined for the wood pellets: expansion values of wheat straw pellets fluctuate in range of 2.8-4.2% from 450--850 °C heating temperature and from 850 °C swelling phenomenon disappears, fig. 7.

Observed final radial shrinkage intensifies exponentially from 2-38.2% for wood particle, from 1.1-26.4% for wood pellet and from 5.3-16.7% for wheat straw pellet with mass loss increase, respectively, from 300-750 °C heating temperature, fig. 7. In range of 700-900 °C heating temperature, it is observed that final shrinkage of biomass samples starts to decrease from 38.2-33.4% for wood particle, from 26.4-21.5% for wood particle and from 16.7-14.7% for wheat straw pellet, fig. 7. Experimental results shows that at high heating temperature formed char starts to expand during shrinking process, what influences final shrinkage decrease. It is considered that during thermal conversion of lignin, char formation takes place and high temperature results in rapid emission of volatiles from formed char. Increased inner pressure stretches overall char structure resulting in char swelling.

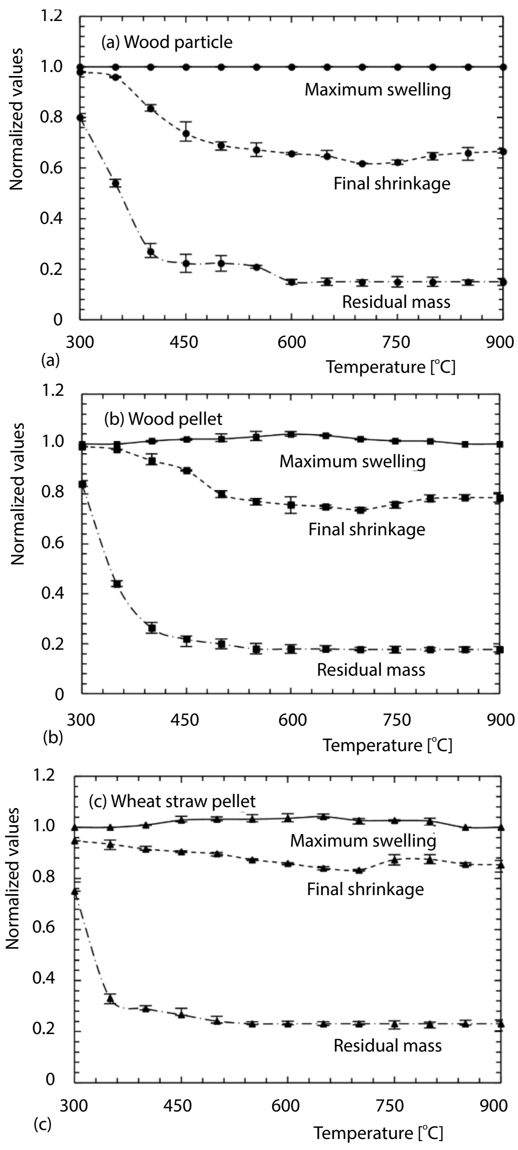

Figure 7. Tendency of biomass thermal deformations at different heating temperature

Regularities of biomass thermal deformations were delineated by the mathematical formulas and parameters for formulas were determined using established data from performed experiments of biomass thermal deformations, see tab. 2.

As the proceeding of biomass thermal deformations depends on the heating temperature, and can be divided into three phases (swelling, shrinkage, and swelling of the residual char), it is ongoing processes are described by three mathematical formulas.

The first mathematical formula evaluates pelletized biomass expansion increasing temperature. An assumption, that expansion of pellets depends on two competing processes, was made for creating formula:

Table 2. Parameters for mathematical formulas of biomass thermal deformations

Parameter	Wood particle	Wood pellet	Wheat straw pellet
D_0, a. u.	–	1	1
D_{S1}, a. u.	–	1.651	1.797
C_1	–	0.01357	0.01
T_1, [°C]	–	600	600
D_{S2}, a. u.	–	1.648	1.4014
C_2	–	0.01417	0.01051
T_2, [°C]	–	567.502	533.501
D_{C1}, a. u.	0.6225	0.73575	0.83233
C_3	0.02087	0.02079	0.01
T_3, [°C]	420.452	456.024	411.669
D_{C2}, a. u.	0.66567	0.73575	0.853
C_4	0.02443	0.0174	10.1406
T_S, [°C]	750	700	700

– The first process is when the volatiles inside the pellet expends its diameter. The intensity of the process can be delineate by first approach with logistic function, eq. (1):

$$f_{P1}(D) = D_0 - \frac{D_{S1} - D_0}{1 + \exp\left[-C_1(T_P - T_1)\right]} \tag{1}$$

– The second process is when the condensed tars on pellet surface are decomposed due to the high temperature and water vapor and volatiles are more easily emitted from pellet center resulting in final swelling decrease. The intensity of this process is described by reverse function, eq. (2):

$$f_{P2}(D) = D_0 - \frac{D_0 - D_{S2}}{1 + \exp\left[-C_2(T_P - T_2)\right]} \tag{2}$$

Since these two processes compete with each other, final expansion of biomass pellets increasing the heating temperature from 300-900 °C is described by average mean of both functions, eq. (3):

$$f_1(D) = \frac{1}{2}\left[f_{P1}(D) + f_{P2}(D)\right] \tag{3}$$

Theoretically calculated and experimentally determined final expansion values of wood pellet and straw pellet with increasing pyrolysis temperature are presented graphically in fig. 8.

Mathematical formulas of biomass shrinkage were delineated by two assumptions. First one, where each moment of time biomass shrinkage progress depends on the current diameter until it reaches the final smallest possible diameter. Therefore, final shrinkage of the diameter can be described in eq. (4):

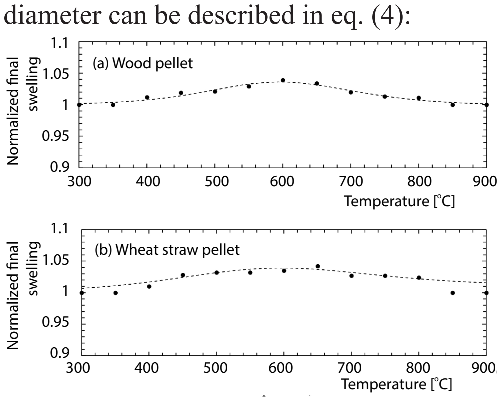

Figure 8. Experimentally determined (dots) and a theoretical calculated (dash line) final expansion values of wood pellet and wheat straw pellet increasing pyrolysis temperature from 300-900 °C

$$f_2(D) = \frac{D_{SV0} - (D_{SV0} - D_{C1})}{1 + \exp^{-C_S(T_P - T_2)}} \tag{4}$$

A second assumption is that if the pyrolysis temperature is higher than 700 °C, residual char begins to expand in the end of biomass shrinkage, and the intensity of char expansion at each moment of time depends on the current size of residual char. The higher the temperature, more intensive char expansion results in shrinkage decrease of final biomass diameter. In this case, biomass final diameter dependence on the pyrolysis temperature above 700 °C, including the influence of char swelling, could be described by eq. (5):

$$f_3(D) = \frac{D_{C1} + (D_{C1} - D_{C2})}{1 + \exp^{-C_4(T_P - T_S)}} \quad (5)$$

Experimentally determined and a theoretical calculated shrinkage values of wood particle wood pellet and wheat straw pellet increasing pyrolysis temperature from 300-900 °C are presented in fig. 9.

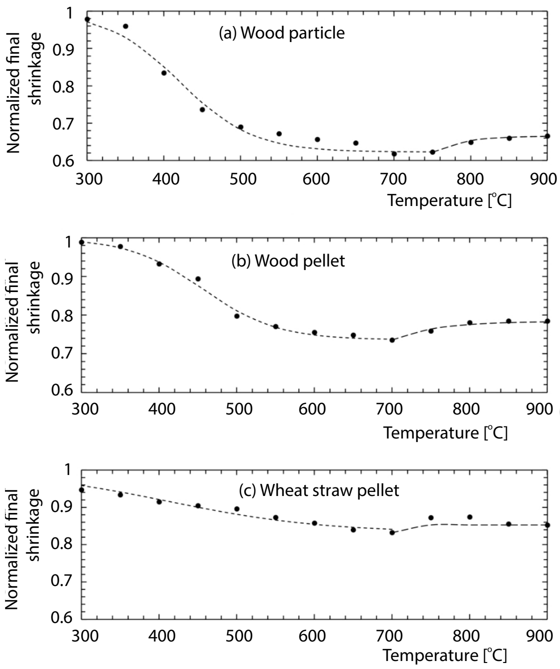

Figure 9. Experimentally determined (dots) and a theoretical calculated (dash line) final shrinkage values of wood particle, wood pellet, and wheat straw pellet increasing pyrolysis temperature from 300-900 °C

Conclusions

In order to obtain a deeper knowledge about thermal deformations of pelletized biomass which cause fuel agglomeration in pyrolysis zone during gasification, a wood particle, a wood pellet and a wheat straw pellet thermal deformations and mass loss has been studied during pyrolysis at various temperatures. According to analyzed results, the results can be summarized as follows:

- At low heating temperature (400 °C), neglible swelling effect of pelletized biomass occurs expanding pellets about 1% with respect to the initial diameter. The swelling phenomenon of pelletized samples intensifies with the heating temperature increase of up to 650 °C causing the maximum expansion by 3.38% for a wood pellet and 3.68% for a wheat straw pellet with respect to the initial diameter. With the heating temperature increasing over 600 °C, the expansion of pellets starts decreasing and disappears when the temperature is higher than 850 °C.
- Pelletized biomass expands during the dehydration process where formed water vapor and volatile compounds inside pellet fail to evaporate from the pellet center due to tar condensation ongoing on the surface which clogs possible ways out. Increasing the heating temperature intensifies tar destruction which relieves release of accumulated compounds with intensified mass loss indicating intensive devolatization process.
- Final shrinkage intensifies exponentially from 16.5-39.6% for a wood particle, from 6.7-26.4% for a wood pellet and from 8.51-16.8% for a wheat straw pellet with the heating temperature increase up to 700-750 °C.
- In the heating temperature range of 700-900 °C, the observed formed char swelling causes relative shrinkage of wood samples to decrease from 40-33 % for a wood pellet and from 27-21 % for a wood particle, and
- Developed mathematical formulas of pelletized biomass thermal deformations correlates with experimental data and could be used predicting pelletized biomass diameter changes increasing temperature in numerical pyrolysis models.

Nomenclature

C_1 – coefficient describing the expansion intensity depending on the type of biomass, [–]
C_2 – coefficient describing the intensity of expansion decrease and depends on the type of biomass, [–]
C_3 – coefficient describing the intensity of shrinkage and depends on the type of biomass, [–]
C_4 – coefficient describing the intensity of shrinkage and depends on the type of biomass, [–]
D_0 – initial diameter of biomass particle, [AU]
D_{C1} – the final diameter of the biomass shrinkage not including residual char expansion and depends on the type of biomass, [AU]
D_{C2} – maximum expansion value of residual char at 900 °C temperature, [AU]
D_{S1} – theoretical biomass expansion value, [AU]
D_{S2} – theoretical biomass particles maximum expansion value, [AU]
D_t – diameter of biomass particle during time
m_t – mass of biomass particle during time
T_1 – temperature of pellet expansion saturation, [°C]
T_2 – temperature of pellet expansion saturation, [°C]
T_3 – pyrolysis temperature at which diameter shrinks to the smallest possible value, [°C]
T_C – center temperature of sample, [°C]
T_P – temperature of pyrolysis, [°C]
T_S – the temperature at which expansion of residual char starts and depends on the type of biomass, [°C]

References

[1] Fantozzi, F., *et al*., Performance Evaluation of the IPRP Technology when Fuelled with Biomass Residuals and Waste Feedstocks, *Proceedings,* ASME Turbo Expo, Orlando, Fla., USA, 2009, Vol. 1, pp. 449-458
[2] Byrne, C. E., Nagle, D. C., Carbonized Wood Monoliths-Characterization, *Carbon, 35* (1997), 2, pp. 267-73
[3] Larfeldt, J., *et al*., Modelling and Measurements of the Pyrolysis of Large Wood Particles, *Fuel, 79* (2000), 13, pp. 1637-43
[4] Davidsson, K. O., Pettersson, J. B. C., Birch Wood Particle Shrinkage during Rapid Pyrolysis, *Fuel, 81* (2002), 3, pp. 263-70
[5] Huang, Q. X., *et al*., Modeling and Experimental Studies of the Effects of Volume Shrinkage on the Pyrolysis of Waste Wood Sphere, *Energy & Fuels, 28* (2014), 10, pp. 6398-406
[6] Pattanotai, T., *et al*., Gasification Characteristic of Large Wood Chars with Anostropic Structure, *Fuel*, *117* (2014), Part A, pp. 331-39
[7] Kumar, R. R., *et al*., Shrinkage Characteristics of Casuarina Wood during Devolatilization in a Fluidized Bed Combustor, *Biomass Bioenergy, 30* (2006), 2, pp. 153-65
[8] Chirone, R., *et al*., Fluidized Bed Combustion of Pelletized Biomass and Waste-Derived Fuels, *Combustion and Flame*, *155* (2008), 1-2, pp. 21-36
[9] Zhou, C., *et al*., A study of the Pyrolysis Behaviors of Pelletized Recovered Municipal Solid Waste Fuels, *Appl Energy*, *107* (2013), July, pp. 173-82

Paper submitted: September 16, 2016
Paper revised: March 9, 2017
Paper accepted: March 9, 2017