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Original Article

Comparative Analysis of Gross Calorific Value by Determination Method of Lignocellulosic Biomass Using a Bomb Calorimeter[1]

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ABSTRACT

This study was conducted to compare and analyze gross calorific values from measurement methods of lignocellulosic biomass and calculation data from calorific value prediction models based on the elemental content. The deviation of *Liriodendron tulipifera* (LT) and *Populus euramericana* (PE) was shown 7.7 cal/g and 7.4 cal/g respectively in palletization method, which are within repeatability limit 28.8 cal/g of ISO FDIS 18125. In the case of Thailand charcoal (TC), nontreatment method and palletization method was satisfied with repeatability limit as 22.8 cal/g and 8.8 cal/g respectively. Seowon charcoal (SC) was shown deviation of 11.4 cal/g in nontreatment method, because the density and chemical affinity of sample increases as the carbon content increases from heat treatment at high temperature in the case of TC and SC. In addition, after applying the elemental content of each of these samples to the calorific value prediction models, the study found that Model Equation (3) was relatively consistent with measured calorific values of all these lignocellulosic biomass. Thus, study about the correlation between the density and size of particle should be conducted in order to select the measurement method for a wide range of solid biofuels in the future.

Keywords : gross calorific value, solid biofuels, lignocellulosic biomass, bomb calorimeter.

1. INTRODUCTION

As the amount of greenhouse gases emission is on the rise, largely due in part to the continuous use of fossil fuels, the effects of climate change, such as global warming, are being observed all around the world. To reduce this change, a new climate regime was launched, with the aim of greenhouse gases reduction. Accordingly, there is growing attention on renewable energy, such as solar power, wind power, hydrogen, hydropower and bioenergy. In particular, solid biofuels, one of the bioenergy technologies, is an abundant resource that is available from all the organic living beings in the natural world, in addition to being renewable and carbon-neutral (Lee *et al*., 2015).

Solid biofuels produced and used from lignocellulosic biomass include woodchips, charcoal and wood pellets, with the quality of such fuels

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varying, depending on their physical properties and chemical composition. Among other physical properties, calorific value could be an important component that indicates the economic value of a solid fuel (Toscano and Pedretti, 2009).

The standard for calorific value measurement in Korea is the Korean Standard's KS E ISO1928, "Solid mineral fuels－Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value". However, this is just limited to solid mineral fuels. The standard to measure the calorific value of solid biofuels is the International Organization for Standardization's ISO FDIS 18125, "Solid biofuels－Determination of calorific value". Its scope includes measuring the gross calorific value of a solid biofuel at the standard temperature of 25℃, with a constant volume of the bomb calorimeter calibrated by the combustion of the standard reagent, benzoic acid, after which the net calorific value is estimated based on the calculation of the elemental composition of the analyzed sample. In addition, according to the European Union's EN 14778, sealed and airtight containers should be used to measure the sample. ISO 14780 states that regarding the particle size of a solid biofuel, the sample should be selected through the standard sieve 18 mesh (1 mm). If the powder is smaller than 18, 35, and 60 mesh (1, 0.5, 0.25 mm), it should be sealed in a combustion bag or capsule for measurement. Furthermore, when the density of a solid biofuel is too low to be measured, 1.0 ± 0.2 g of a powdered sample should be shaped, at a pressure of 10 t, into a pellet whose diameter is 13 mm before it is measured. Finally, for the repeatability limit, the same operator should perform the measurement with the same apparatus and sample in the same laboratory, shortly after the original measurement. Moreover, the differences in the repeated results should be no more than 120 J/g (28.8 cal/g) for wood pellet or sawdust and no more than 140 J/g (33.6 cal/g) for other solid biofuels. For the reproducibility limit, it has been stated that samples should be extracted from the same source at the last stage of sampling preparation, with the differences in the results measured in the two different laboratories being not more than 300 J/g (72 cal/g) for wood pellet or sawdust and no more than 400 J/g (96 cal/g) for other solid biofuels.

However, measuring their calorific value using the preparation methods for the analysis samples described above has some complications, as there is a relatively larger error in terms of repeatability when the calorific value of lignocellulosic biomass is measured, as incomplete combustion could occur inside the container or a shut-off ring of the bomb calorimeter lid could burn due to the density of each lignocellulosic biomass, their particle size and the heat treatment of lignocellulosic biomass. In this regard, this study used the calorimeter Parr 6400 (Parr, USA) for comparing and analyzing the results measured by powder, oil paper and gelatin capsule sealing, as well as pelletization in accordance with ISO FDIS 18125, in order to identify a measurement method that satisfies the repeatability limit when untreated and heat-treated lignocellulosic biomass are measured.

2. MATERIALS and METHODS

2.1. Materials

This study used *Liriodendron tulipifera* (LT), *Populus euramericana* (PE), Thailand charcoal (TC) and Seowon charcoal (SC) that is manufactured in Hoengseong County, Gangwon Province, South Korea. LT and PE were processed into chips by the Korea Forest Research Institute's disc chipper (Yulim, South Korea). The LT woodchips thus produced were used in raw form, while the PE woodchips were put into the torrefaction reactor (Drying technology, South Korea) and heat-treated at 260℃ for 30 min. Each of those woodchips, as well as TC and SC, were ground using a household blender, after which the standard sieve 60 mesh (250 μm) was used for selection. Before the calorific value was measured, the sample was dried in the oven at 105 ± 3℃ for 24 h and then cooled in a desiccator for 30 min to the ambient temperature, before being analyzed.

2.2. Calorific Value Measurement

The calorimeter Parr 6400 (Parr, USA) was used to measure the calorific value. Before measurement, the standard reagent, benzoic acid, was used to calibrate the calorimeter. The sample was shaped and measured five times each, in the form of powder, oil paper sealing, gelatin capsule sealing and pellet.

2.2.1. Nontreatment Measurement Method

Nontreatment method is described in Fig. 1(a). About 0.4-0.5 g of the sample was precisely weighed, placed in a combustion dish and measured, while a powder connected to the ignition wire was in contact with the top of the powder contained in the combustion dish.

2.2.2. Oil Paper Sealing Measurement Method

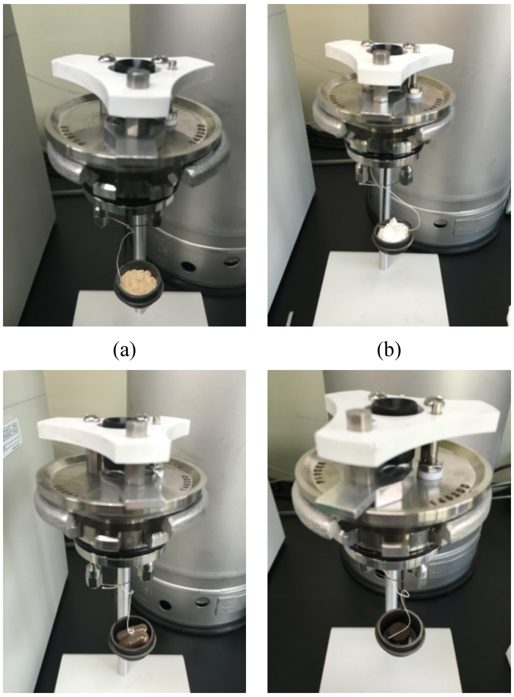
Oil paper sealing method is shown in Fig. 1(b). The oil paper used for measurement (Fisherbrand^{TM}, USA) was 76 mm × 76 mm in size and was not hygroscopic. The calorific value of the oil paper was measured five times repeatedly and the average of those values was used. About 0.4-0.5 g of powder was precisely scaled and placed on the oil paper, after which it was measured by sealing the powder to prevent it from leaking, placing it in the combustion dish and attaching a powder connected to the ignition wire, to the top of the oil paper. Finally, the oil paper's average calorific value was subtracted.

2.2.3. Gelatin Capsule Sealing Measurement Method

The gelatin capsule sealing method is shown in Fig. 1(c). The volume capacity of the gelatin capsule used in the measurement (Torpac®, USA) was 0.95 ml, while the measurement method was the same as that mentioned for oil paper.

Table 1. Model equations for GCV calculation

Number	Ref.	Model Equation (HHV, cal/g)
(2)	[7]	$GCV = 84\ C + 277.65\ H + 25\ S - 26.5\ O + 15\ N$
(3)	[8]	$GCV = 81.43\ C + 315.99\ H + 16.33\ S - 3.66\ Ash - 28.63\ (N + O)$
(4)	[9]	$GCV = 78.39\ C + 341.92\ H - 5.66\ N + 22.2\ S - (1\text{-}Ash/100)\ (9586.52\ H/C) + 82.84$
(5)	[10]	$GCV = [363.5\ H/(100 - Ash) + 235.9]\ [\ C/3 + H - O/8 + S/8]$



(a) (b)

(c) (d)

Fig. 1. Method for determination of the calorific value. (a) Nontreatment method (LT), (b) Oil paper sealing method (PE), Gelatin capsule sealing method (TC), (d) Pelletization method (SC).

2.2.4. Pelletization Measurement Method

Pelletization method is shown in Fig. 1(d). For pelletization, the study used a pellet die (MACRO/MICRO 13 mm KBr DIE, International Crystal Laboratories, USA), capable of shaping according to the diameter suggested in ISO FDIS 18125. About 0.4-0.5 g of powder was placed in the die, compressed at a pressure of 10 t by the hydraulic press used for the experiment (Carver, Inc., USA), and converted into a pellet before it was measured. However, SC had a low binding capacity, which is why it was not pelletized.

2.3. Ash and Elemental Content Analysis

The ash and elemental content of the lignocellulosic biomass were analyzed in accordance with ISO 18122:2015. Using the vario MICRO cube elemental analyzer (elementar, Germany) for elemental content analysis, the study quantitatively analyzed the content of C, H, N, and S. The process was repeated 3 times. 2693 (NIST, USA) was used as the standard substance in the analysis. The content of O was calculated based on Equation (1):

$$O(\%) = 100 - (C + H + N + S + Ash) \cdots\cdots (1)$$

2.4. Calorific Value Prediction Models

Calorific value prediction models applied in this study are listed in Table 1. Each of these models was developed as follows. Equation (2) was developed based on Boie’s correlations

Table 2. Gross calorific value by determination method and species

Sample	Method			
	Powder	Oil paper	Gelatin capsule	Pellet
	Gross calorific value (cal/g)			
LT	4,608.8 (146.7)$^{1,\ b}$	4,633.7 (156.3)$^{a,\ b}$	4,675.0 (261.3)$^{a,\ b}$	4,661.3 (7.7)$^{a,\ b}$
PE	5,141.8 (171.8)$^{a,\ b}$	5,131.7 (47.3)^{b}	5,404.7 (480.8)$^{a,\ b}$	5,217.2 (7.4)$^{a,\ b}$
TC	6,031.6 (22.8)^{b}	6,029.0 (37.6)^{b}	6,355.3 (278.1)$^{a,\ b}$	6,083.5 (8.8)^{b}
SC	7,438.2 (11.4)^{a}	7,339.0 (43.4)^{b}	7,465.1 (14.7)^{a}	ND[2]

[1] Mean ± standard deviation

[2] Not determined

Numbers followed by the same letter in each column do not differ statistically ($P < 0.05$) according to Duncan multiple comparison test

among the calorific values of various organic fuels Sheng and Azevedo, 2005), while Equation (3) was developed based on many different calorific prediction models from Mason and Gandhi (Mason and Gandhi, 1983), along with the analysis of a wide range of coals. Equation (4) was developed based on Graboski and Bain's correlations between the elemental analysis of lignocellulosic biomass and combustion reaction (Graboski and Bain's, 1979), while Equation (5) was developed based on Grummel and Davis's assumption that the heat emitted from the complete combustion of a fuel is in proportion with the amount of oxygen consumed during the combustion (Ronsch and Wagner, 2012).

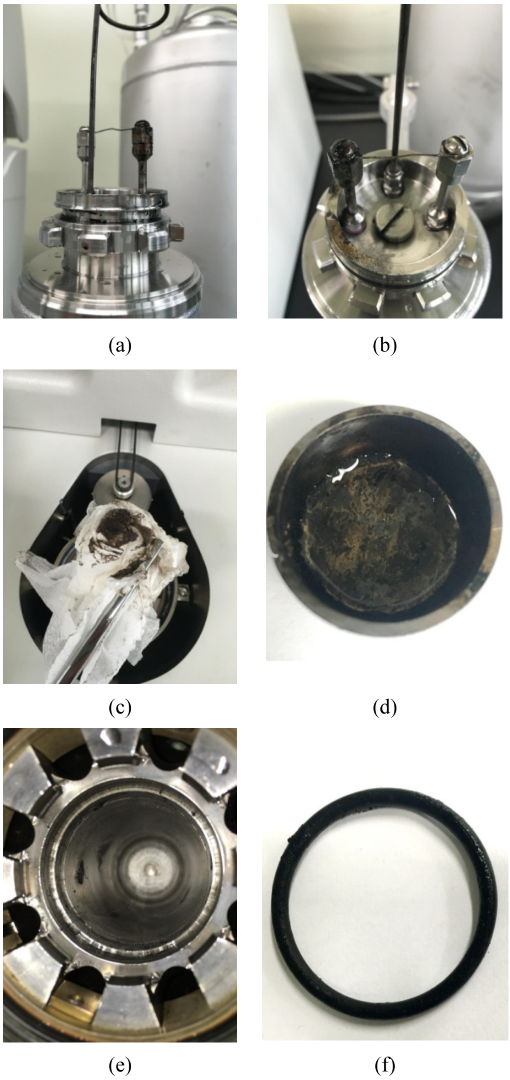
3. RESULTS and DISCUSSION

3.1. Calorific Value Analysis Based on the Measurement Method

The measured calorific values and standard deviations of LT, heat-treated PE, TC and SC, based on powder, oil paper sealing, gelatin capsule sealing and pelletization, are shown in Table 2.

3.1.1. Nontreatment Measurement Method

The measured average calorific values for LT, heat-treated PE, TC and SC, based on non-treatment, were 4608.8 cal/g, 5141.8 cal/g, 6031.6 cal/g and 7438.2 cal/g, respectively. However, the standard deviations for LT and heat-treated PE were 146.7 cal/g and 171.8 cal/g, respectively, indicating that the results exceeded the repeatability limit of 28.8 cal/g, mentioned in ISO FDIS 18125. On the other hand, the standard deviations of TC and SC were 22.8 cal/g and 11.4 cal/g, respectively, indicating relatively reliable deviations. Such large errors could be attributed to the fact that, since LT and heat-treated PE had relatively lower density than TC and SC, they did not undergo combustion inside the container or latch onto the shut-off ring of the bomb calorimeter because of the dispersion of powdered particles all of a sudden, when the ignition wire was ignited for calorific value measurement (Fig. 2).



(a) (b) (c) (d) (e) (f)

Fig. 2. Problems caused during the calorific value determination. (a ∼ e) Unburned residue, (f) burned O-ring.

3.1.2. Oil Paper Sealing Measurement Method

The measured average calorific values, based on oil paper sealing, were 4633.7 cal/g, 5131.7 cal/g, 6029.0 cal/g and 7339.0 cal/g. Unlike the nontreatment results, however, standard deviations were unreliable in all of the samples. Such results is considered to be due to the variation (19.7 cal/g) of calorific value of the oil paper and the incomplete combustion of the oil paper in combustion dish as shown in Fig. 2(d).

3.1.3. Gelatin Capsule Sealing Measurement Method

The average calorific values measured, based on gelatin capsule sealing, were 4675.0 cal/g, 5404.7 cal/g, 6355.2 cal/g and 7465.1 cal/g. LT, heat-treated PE and TC showed unreliable standard deviations of 261.3 cal/g, 480.8 cal/g and 278.1 cal/g, respectively, while SC showed a relatively reliable deviation of 14.7 cal/g. Such results were obtained because gelatin capsules had standard deviations of calorific values like those of oil paper and stuck to the wall of the container as described in Fig. 2. (c) and (f), although they suppressed the dispersion of powder more than oil paper.

3.1.4. Pelletization Measurement Method

Except for SC, the average calorific values measured, based on pelletization, were 4661.3 cal/g, 5217.2 cal/g and 6083.5 cal/g, respectively, while the standard deviations were 7.7 cal/g, 7.4 cal/g and 8.8 cal/g, indicating generally reliable results. These results were attributed to the fact that the ether bond among OH in the powder particles (Kim and *et al.*, 2015), which is formed when they are compressed at a high pressure during pelletization, prevented the dispersion phenomenon, which could occur at the time of ignition, when the calorific value was measured, resulting in com-

Table 3. Elemental analysis and GCV calculation data

Species	Elemental content (% dry basis)					Ash (%)	Experiment	eq. 2	eq. 3	eq. 4	eq. 5
	C (%)	H (%)	N (%)	S (%)	O (%)		GCV (cal/g)				
LT	49.2 (0.3)[1]	6.2 (0.0)	0.6 (0.0)	0.0 (0.0)	44.0 (0.3)	1.1 (0.1)	4,661.3 (7.7)	4,699.9 (27.7)	4,688.0 (25.4)	4,864.9[*] (26.8)	5,845.4[*] (19.3)
PE	55.4 (0.3)	5.8 (0.0)	0.9 (0.0)	0.0 (0.0)	37.9 (0.3)	2.1 (0.1)	5,217.2 (7.4)	5,259.4 (34.3)	5,213.9 (34.3)	5,402.0[*] (28.1)	6,222.5[*] (28.4)
TC	67.7 (0.3)	4.2 (0.0)	0.3 (0.0)	0.0 (0.0)	27.9 (0.3)	3.5 (0.2)	6,083.5 (8.8)	6,106.7 (41.1)	6,018.2 (42.1)	6,228.0 (30.6)	6,711.8[*] (35.8)
SC	92.1 (0.2)	0.5 (0.1)	0.7 (0.0)	0.0 (0.0)	6.7 (0.3)	3.4 (0.1)	7,438.2[*] (11.4)	7,716.0 (45.2)	7,451.2 (49.2)	7,424.4 (34.8)	7,426.3 (42.9)

[1] Mean ± standard deviation

[*] The values significantly different from experimental data

plete combustion.

3.2. Comparison with Calorific Values calculated by the Elemental Content

The elemental content and the calculation results of the calorific value prediction models for each wood spices are shown in Table 3. To compare with the predicted results, pelletization was selected for LT, heat-treated PE and TC, while nontreatment was selected for SC. Comparison between measured calorific values and calorific values predicted by the model equations indicated that LT and heat-treated PE tended to be consistent for Model Equations (2) and (3). TC showed similar results for Model Equations (2), (3) and (4), while SC showed consistency in Model Equations (3), (4) and (5). Considering these results, Model Equation (3) was close to the measured calorific values in all of the wood species in this study. The reason could be that this equation was developed based on the correlations between the lignocellulosic biomass and the combustion process. Therefore, the calorific values from pelletization, which were used for more precise measurement through the bomb calorimeter in this experiment, were considered consistent with those estimated based on the elemental content.

4. CONCLUSIONS

In this study, the gross calorific values were compared and analyzed four selected lignocellulosic biomass, based on four measurement using the bomb calorimeter. LT and heat-treated PE showed results that satisfied the repeatability limit (28.8 cal/g) suggested in ISO FDIS 18125 in the case of palletization method. TC showed satisfied results with nontreatment method and palletization method, while SC showed such results with nontreatment method and gelatin capsule sealing method. In conclusion, TC and SC showed to produce satisfied results with nontreatment method, as they were dispersed relatively less than LT and PE during ignition, because they were already heat-treated at a high temperature, which increased their carbon content and density. In addition, in comparison with the calorific value prediction models, Model Equation (3), based on lignocellulosic biomass, showed relatively consistent results with the measured results in all the wood species. For the future, studies and experiments are planned in order to find an appropriate measurement method considered the density of powder samples and the particle size suggested in ISO FDIS 18125.

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