

Use of Statistical Methods for Minimizing the Error in Measuring the Energy Content of Agricultural Waste by Using Bomb Calorimeter and Suggestions for their Use in Electricity Production

Fotini Kogia^{1,*}, Georgia Sapalidou¹ and Stavros Karampatzakis¹

¹E.M.T. Institute of Technology, Electrical Engineering T.E., Kavala, Greece

Received 24 September 2019; Accepted 26 February 2020

Abstract

In the present work agricultural crop waste such as walnut shells and peach kernels are used, and an assessment of their energy content using a calorimeter bomb is done. For this purpose, ten different masses of the same sample are burned in a bomb calorimeter and their energy content is measured. The measurement for each mass is carried out at least three times. The total number of measurements for two different samples of agricultural waste is at least sixty. The measurements done for each sample show the values of the temperature in the bomb calorimeter's bucket and the energy content of the sample. For each sample, the procedure is described below. We calculate the average temperature and using the Least Squares Method (LSM), we calculate the energy content of the sample with the possible least error. Finally, for the measured values, the Gaussian Dispersion curve is plotted from which the accuracy of the bomb calorimeter measurements is obvious. The same procedure is performed for both samples under study. From the values of the energy content of the samples and from the residue during their burning, a comparative evaluation of the samples is made concerning the possibility of their utilization for electricity generation.

Keywords: Least Squares Method; Gaussian Distribution; measurement error; gross heat; electrical power.

1. Introduction

Bomb calorimeter is a high accuracy instrument with which the energy content of several materials can be measured. Agricultural waste has significant energy value and could well replace conventional fuels for electricity production [1].

In the present work, energy content of agricultural crop waste such as walnut shells and peach kernels were measured using automatic isoperibol calorimeter Parr 6400 in International University of Greece Physics Laboratory in Kavala, Greece and the results were very encouraging [2]. In particular, it was found that the energy content of walnut shells is equal to 4332 cal/g, whereas for peach kernels an energy content equal to 4790 cal/g was found. The energy corresponding to one tone of walnut shells is enough to feed a four-member family with the electrical energy it consumes in one year, while one tone of peach kernels could cover its electricity needs for more than one year.

2. Material and method

2.1 Materials used and data obtained

All measurements were carried out in the Physics Laboratory of the Department of Physics of the International

University of Greece in Kavala using the Parr 6400 bomb calorimeter, with which the energy content of each sample was measured. Benzoic acid is always used at the beginning of a cycle of measurements for the calibration of the instrument [1]. Samples (walnut shells and peach kernels) are cut in very small pieces and pressed to form pellets before being burned in the calorimeter [3, 4].

Benzoic acid has a very stable energy content of 6318 cal/g and is thus used both for the calibration of the bomb calorimeter and for finding its heat capacity (here it was found equal to 927 cal/grad). The presentation of the aforementioned procedures goes beyond the scope of this paper and is omitted.

Following the experimental procedure required to obtain the experimental measurements, tables 1 and 2 for walnut shells are completed [5, 6].

Table 1. Energy content of walnuts shells

#	Sample ID	Energy content (GH), (cal/g)	Residue
1	NUTS-SHELL-1	4333,9884	Clear water, tiny gray balls, zero ash
2	NUTS-SHELL-2	4336,0371	Little ash and lightly beige water
3	NUTS-SHELL-3	4339,5926	Clear water, tiny gray balls, zero ash
4	NUTS-SHELL-4	4328,0174	Zero ash and clear water
5	NUTS-SHELL-5	4330,0478	Zero ash and clear water
6	NUTS-SHELL-6	4329,0726	Little ash and lightly

*E-mail address: fkogia@teiemt.gr

ISSN: 1791-2377 © 2020 School of Science, ITHU.

All rights reserved.

7	NUTS-SHELL-7	4337,1730	beige water Little ash and lightly beige water
8	NUTS-SHELL-8	4338,4394	Little ash and lightly beige water
9	NUTS-SHELL-9	4335,0249	Zero ash and clear water
10	NUTS-SHELL-10	4339,0305	Zero ash and clear water

Table 2. Sample mass and temperature change for walnuts shells

#	Sample ID	Sample mass m _s (g)	Temperature change ΔT (°C)
1	NUTS-SHELL-1	2,8088	13,1401
2	NUTS-SHELL-2	1,8702	8,7075
3	NUTS-SHELL-3	1,5642	7,3006
4	NUTS-SHELL-4	1,4115	6,5718
5	NUTS-SHELL-5	1,2823	5,9708
6	NUTS-SHELL-6	1,1112	5,1737
7	NUTS-SHELL-7	1,0005	4,6612
8	NUTS-SHELL-8	0,9812	4,5921
9	NUTS-SHELL-9	0,9541	4,4422
10	NUTS-SHELL-10	0,5021	2,3399

Tables 3 and 4 for peach kernels measurements are completed.

Table 3. Energy content of peach kernels

#	Sample ID	Energy content (GH) _s (cal/g)	Residue
1	PEACH-1	4797,0432	No residue
2	PEACH -2	4750,1230	No residue
3	PEACH -3	4768,1415	No residue
4	PEACH -4	4750,7643	No residue
5	PEACH -5	4778,1013	No residue
6	PEACH -6	4740,9700	No residue
7	PEACH -7	4784,3103	No residue
8	PEACH -8	4774,0429	No residue
9	PEACH -9	4768,5119	No residue
10	PEACH -10	4794,9104	No residue

2.2 Experimental procedure and data process

The measurements for each sample are repeated three times for each mass and their average value for mass and for energy content is estimated from the formula:

$$\bar{x} = \sum_{i=1}^N x_i \tag{1}$$

Then, using the Least Squares Method (LSM), the energy content of the sample with the possible least error can be estimated, from equation (2) [7, 8].

$$\Delta T = \frac{(GH)_s}{k_c} \cdot m_s \tag{2}$$

where k_c is bomb calorimeter heat capacity, ΔT is the water's in the bomb calorimeter temperature rise, (GH)_s is sample energy content and m_s is sample mass.

By matching (2) with the equation of the straight line where m_s→x, ΔT→y, it is obtained that:

$$a=0 \text{ and } b = \frac{(GH)_s}{k_c} \tag{3}$$

By using LSM for the measurements taken, the energy content of each sample can be estimated. It is known (it was found previously) that the bomb calorimeter heat capacity is equal to 927 cal/grad (tables 5 and 6 and figures 1 and 2).

Table 4. Sample mass and temperature change for peach shells

#	Sample ID	Sample mass m _s (g)	Temperature change ΔT (°C)
1	PEACH -1	2,6277	13,6041
2	PEACH -2	2,4440	12,5950
3	PEACH -3	2,0012	10,3210
4	PEACH -4	1,9991	10,2121
5	PEACH -5	1,8282	9,4112
6	PEACH -6	1,6010	8,2012
7	PEACH -7	1,3456	6,9368
8	PEACH -8	1,0021	5,1614
9	PEACH -9	0,9568	4,9121
10	PEACH -10	0,9312	4,8031

Table 5. LSM for walnut shells

#	x	y	x ²	x·y
1	2,8088	13,1401	7,8894	36,9079
2	1,8702	8,7075	3,4976	16,2848
3	1,5642	7,3006	2,4467	11,4196
4	1,4115	6,5718	1,9923	9,2761
5	1,2823	5,9703	1,6443	7,6557
6	1,1112	5,1737	1,2348	5,7490
7	1,0005	4,6612	1,0010	4,6635
8	0,9812	4,5921	0,9103	4,2383
9	0,9541	4,4422	0,9103	4,2383
10	0,5021	2,3399	0,2521	1,1749

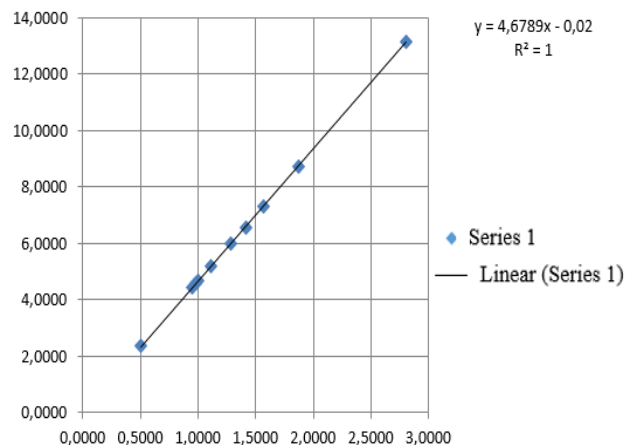


Figure 1. LSM graph for walnut shells

Table 6. LSM for peach kernels

#	x	y	x ²	x·y
1	2,6277	13,6041	6,9048	35,7475
2	2,4440	12,5950	5,9731	30,7822
3	2,0012	10,3210	4,0048	20,6544
4	1,9991	10,2121	3,9964	20,4150
5	1,8282	9,4112	3,3423	17,2056
6	1,6010	8,2012	2,5632	13,1301
7	1,3456	6,9368	1,8106	9,3342
8	1,0021	5,1614	1,0042	5,1722
9	0,9568	4,9121	0,9155	4,6999
10	0,9312	4,8031	0,8671	4,4726

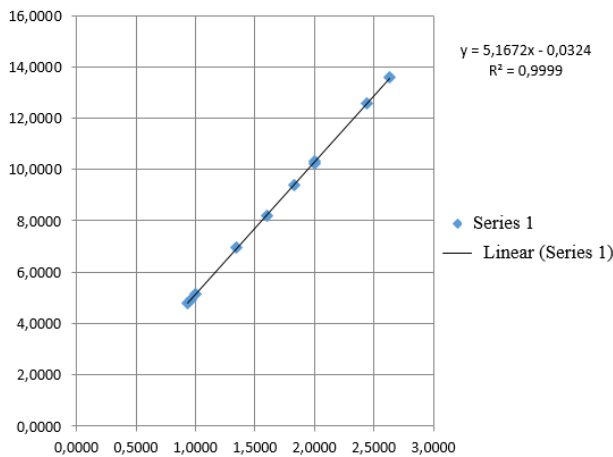


Figure 2. LSM graph for peach kernels

In the statistical analysis of experimental data, to determine the accuracy of the measurements and thus the correct choice of the measurement method and the correct operation of the measuring instrument, the graph of the normal distribution (Gaussian distribution) is widely used.

For plotting the normal distribution graph, the equations (4), (5), (6) and (7) are used. Equation (4) is used for the estimation of the standard deviation or standard error of the distribution

$$\sigma_x = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}} \tag{4}$$

where x_i is each one of the measured values, \bar{x} is the mean of the measured values and N is the total number of measurements.

Equation (5) is used for the estimation of the normal distribution or Gaussian distribution

$$\rho_x(x) = \frac{1}{\sigma_x \cdot \sqrt{2\pi}} \cdot e^{-\frac{(x_i - \bar{x})^2}{2\sigma_x^2}} \tag{5}$$

where σ_x is the standard deviation or standard error of the distribution given from (4).

For walnut shells

$$\sigma_x = 4,295 \text{ and } \rho_x(x) = 0,0929 \cdot e^{-\frac{(x_i - 4335)^2}{36,888}} \tag{6}$$

thus for peach kernels

$$\sigma_x = 18,953 \text{ and } \rho_x(x) = 0,0211 \cdot e^{-\frac{(x_i - 4771)^2}{718,444}} \tag{7}$$

3. Results and discussion

Using LSM it is easy and accurate to confirm the validity of experimental research data and from normal distribution graph this accuracy becomes obvious.

For walnut shells using LSM it is found $a = - 0,0200$ and $b = 4,6789$ from which and from equations (3) it derives that $(GH)_s = 4337,3403$ cal/g. The mean for the energy content values measured by bomb calorimeter for walnut shells, derives from table 1 and equation (1), and it is equal to 4334,6424 cal/g.

In figure 3 it is shown the normal distribution graph for walnut shells.

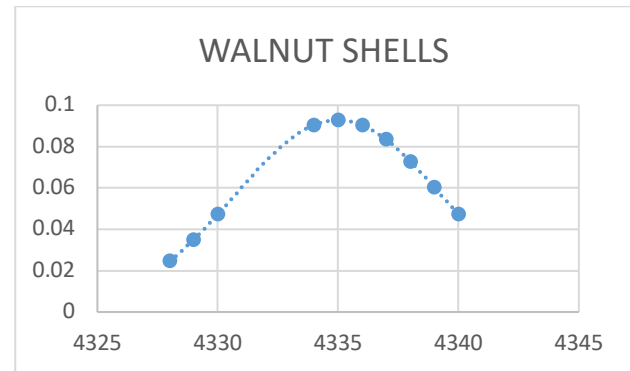


Figure 3. Walnut shells normal distribution

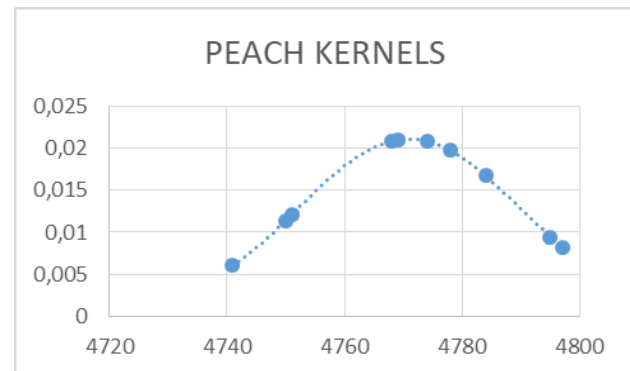


Figure 4. Peach kernels normal distribution

For peach kernels using LSM it is found $a = - 0,0324$ and $b = 5,1672$ from which and from equations (3) it derives that $(GH)_s = 4789,9944$ cal/g. The mean for the energy content values measured by bomb calorimeter for peach kernels, derives from table 3 and equation (1), and it is equal to 4770,6919 cal/g.

In figure 4 it is shown the normal distribution graph for peach kernels.

For comparison, the values of the energy content of certain agricultural crop waste are listed in the tables 7 and 8 as measured in our laboratory by the Parr 6400 bomb calorimeter [9].

Table 7. Experimental results for energy content of nutshells [10]

Nut	Energy content of nutshells (cal/g)	Residue
Walnuts	4333,9884	Clear water, tiny gray

Peanuts from Aegina	4149,5384	balls, zero ash Clear water, little ash
Sunflower seeds	4307,6732	Lightly beige water, invisible tiny balls, minimal ash
Peanuts (arapika)	Misfire condition	-

Table 8. Experimental results for energy content of fruit kernels [10]

Fruit	Energy content of fruit kernels (cal/g)	Residue
Apricot	5602,4163	No residue
Peach	4797,0432	No residue
Plum	4971,5181	No residue
Grape	4865,6296	Enough ash
Apple	5400,1982	Enough ash
Watermelon	5476,7803	A little gray residue, no ash
Melon	5446,6373	Minimal residue gray, no ash

A four member family consumes annually 5000 kWh of electrical energy. The energy content of walnut shells is found equal to 4337 cal/g. Given that 1 cal = 1,163·10⁻⁶ kWh, it can be found that from one tone of walnut shells the above family won't need to pay for electrical energy for 368 days that is for 1 year and 3 days.

For peach kernels (4790 cal/g) correspondently the duration will be 407 days that is 1 year 1 month and 12 days.

4. Conclusions

Bomb calorimeter is a high accuracy instrument for measuring the energy content of materials (solid, liquid and air state). This is confirmed from the measurement of energy content of samples (walnut shells and peach kernels) and from the statistical analysis of them (LSM graph, standard deviation and normal distribution).

From the measurements of energy content of the samples used in present work it derives the conclusion that walnut shells, peach kernels and the same agricultural waste generally, taking under account the residue of their burn, are very suitable for electricity production.

More specifically the energy corresponding to one tone of walnut shells is enough to feed a four members family (5000 kWh annually and 1 cal = 0,000001163 kWh) with the electrical energy it consumes in one year, while one tone of peach kernels could cover its electricity needs for more than one year.

Acknowledgements

This study was supported by the advanced research laboratory Hephaestus and by Physics Department of International University of Greece, in Kavala. The instrument used is the Parr 6400 bomb calorimeter located at Physics Laboratory.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License



References

1. Gravalos I., Xyradakis P., Kateris D., Gialamas T., Bartzialis D., Giannoulis K., An experimental determination of Gross Calorific Value of different agroforestry species and bio-based industry residues, National Resources, 7, 2016, pp. 57–68.
2. [https://www.scirp.org/pdf/NR_2016012216040930.pdf]
3. Parr Instrument Company, 6400 Oxygen Bomb Calorimeter, Operating instruction manual, for models produced after October 2010.
4. [http://www.manualsdir.com/manuals/740358/parr-instrument-6400.html]
5. J. O. Awulu, P. A. Omale, J. A. Ameh, Comparative Analysis of Calorific Values of Selected Agricultural Wastes, Nigerian Journal of Technology, Vol. 37, No. 4, October 2018, pp. 1141-1146.
6. [https://www.researchgate.net/publication/328531226_Comparative_analysis_of_calorific_values_of_selected_agricultural_wastes]
7. R. Picchio, R. Spina, A. Sirna, A. Lo Monaco, V. Civitarese, A. Del Giudice, A. Suardi, L. Pari, Characterization of Woodchips for Energy from Forestry and Agroforestry Production, Energies, Vol. 5, 2012, pp. 3803-3816.
8. [https://pdfs.semanticscholar.org/3554/7d5e4377fe9d28b0c638ec58a5811c6d210d.pdf]
9. A. Brunerova, M. Brozek, Is it Advantageous to Reuse Fruit Waste Biomass from Processing of Grapevine (Vitis Vinifera L.) for Briquette Production?, Engineering for Rural Development, Jelgava, 24-26/05/2017, pp. 555-560.
10. [http://www.tf.llu.lv/conference/proceedings2017/Papers/N109.pdf]
11. A. Brunerova, J. Malatak, M. Müller, P. Valasek, H. Roubik, Tropical Waste Biomass Potential for Solid Biofuels Production, Agronomy Research 15 (2), 2017, pp. 359–368.
12. [https://www.researchgate.net/publication/316964556_Tropical_waste_biomass_potential_for_solid_biofuels_production]
13. A. Karagounis, Use of Least Squares Method for minimizing the error in the measurement of the energy content of tsipouro using bomb calorimeter, graduate thesis, supervisor Fotini Kogia, EMMATECH, 2017, pp. 54–66.
14. J. Samakovlis, Fact-finding study for operation consumables of bomb calorimeter saving and statistical control of reliability of measurements, graduate thesis, supervisor Fotini Kogia, EMMATECH, 2017, pp. 44–53.
15. F. Kogia, K. Andronikopoulos, G. Sapalidou, P. Angelidis, Gr. Angelidis, Using Least Squares Method for Minimizing the Total Energy Value Measurements Error for Olive Oil and Alcoholic Beverages with Bomb Calorimeter, 3rd IMEKOFODS, Metrology Promoting Harmonization & Standardization in Food & Walnutrition, Thessaloniki, Greece, 1-4/10/2017, pp. 170-173.
16. [https://www.imeko.org/publications/tc23-2017/IMEKO-TC23-2017-048.pdf]
17. G. Amoako, P. Mensah-Amoah, Determination of Calorific Values of Cocowalnut Shells and Cocowalnut Husks, Journal of Materials Science Research and Reviews, 2 (2), 2019, pp.1-7.
18. [https://www.researchgate.net/publication/329894161_Determination_of_Calorific_Values_of_Cocowalnut_Shells_and_Cocowalnut_Husks]