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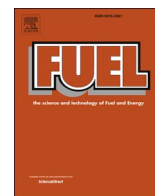
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Full Length Article

Model-free measurements of calorific content and ash content of mixed garden wastes using a bomb calorimeter

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ABSTRACT

Two of the most important properties of a material to determine its suitability as a waste-to-energy feedstock are its calorific content and ash content (AC). In the literature, it has been widely suggested that using the results from ultimate and proximate analysis to determine the former through empirical models is an accurate method that saves time and reduces labor. In this work we evaluated the suitability of these models for mixed garden waste using samples collected from two geographical distinct municipal waste disposal sites. It was found that when the models, with parameters given in the literature, are used, the errors in the estimates of higher heating values (HHV) could be higher than acceptable limits. Using linear regression, we determined the model parameters for our specific feedstocks based on the measured elemental, AC and the HHV values from a bomb calorimeter that reduced this error, with AC being the best predictor. However, there were still points with errors over 15%, indicating that these empirical models may not be suitable for the highly varying biomass characteristics typical of mixed green waste feedstocks and that direct measurement through bomb calorimetry still provides the most accurate results. We did find though, that the residues from bomb calorimetry could be used to determine the ash content of mixed garden waste as a time-, labor- and energy-saving measure. Standards for ash content measurements involve the use of a furnace. Here we compared two standard procedures to each other and to the bomb calorimeter residue. Statistical analysis explicitly showed for the first time that we are aware of, that the residue of mixed garden waste from bomb calorimetry tests provided a reliable estimate of ash content over a large range with agreement within 10 % to standards and therefore can be used in place of the standards thereby significantly reducing the time and cost of the tests while getting more accurate results for HHV compared to the models suggested in the literature.

1. Introduction

The calorific content and ash content (AC) of a biomass material are two of its most important properties regarding its utility as a fuel source. The calorific content, which is commonly reported as the higher heating value (HHV) since it can be directly measured, indicates the maximum amount of energy output that can be expected on a per mass basis. The standard for measuring HHV is by calorimetry [1–3]. Essentially this involves the complete combustion of a biomass sample in a bomb calorimeter in a pressurized, oxygen-rich environment. It is a key indicator of the suitability of the biomass as a fuel [4] and is an important parameter for designing and analyzing biomass-based thermal and electrical generation systems [5,6].

Alternatively, researchers have developed models to estimate HHV using data from proximate analysis [6–9], ultimate (elemental) analysis [5,10], structural analysis [11] or combinations of ultimate and

proximate analysis [12]. Though numerous correlations have been developed, there are issues which make their use problematic [13]. The correlations are based on data from multiple biomass types without considering variations between biomasses [5,14–16], so for accurate estimations, mathematical models have to be developed for a particular biomass system [10]. As municipal garden is made up of unknown plants and contaminated with soils and other debris by its nature, this composition can change daily. Therefore, modeling would not be expected to accurately predict the HHV of the material since it would require being constantly updated and verified with bomb calorimetry. Both tests can result in sampling errors owing to the small sample sizes used, so for accurate results of the entire piles multiple tests would be needed from different physical locations within the piles. However, here we are only interested in determining the accuracy of the tests themselves that would be used for measuring the samples taken.

The justification for the use of such empirical models was that

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calorimetry required expensive equipment and the experimental procedure was complicated and time-consuming and thus very costly compared to carrying out proximate, ultimate or structural analysis [13,17,18]. While this was historically the case, currently there are commercially available calorimeters which are simple to use and require no more labor intervention than an elemental analyzer. Velázquez-Martí et al., (2017) conducted a cost analysis and concluded that determining HHV using an elemental analyzer combined with a mathematical model was 23% cheaper (per sample) than the direct determination using a bomb calorimeter [10]. Examining their analysis, the main contributor to the increased cost of the latter was labor cost due to sample analysis time (5 min per sample for the elemental analyzer vs. 20 min for the bomb calorimeter). However, the elemental analyzer is more than 2 times the cost of a bomb calorimeter (€125,000 vs €50,000). Consumable costs were also lower for the bomb calorimeter. Given capital costs play a major role in choosing an equipment, the calorimeter may be a more attractive choice. Furthermore, the potential benefits of higher accuracy of the direct measurement due to improvements in process operations should be considered.

Ash is the inorganic residue remaining after combustion. As it does not contribute to the energy released by burning the biomass, it reduces energy output, with an increase in ash content indicating a decrease in heating value [19]. Furthermore, ash can result in slag formation and fouling which will lead to higher resistance to heat transfer and cause damage to combustion equipment as well cause operational problems [4,20]. High AC can also lead to incomplete combustion [21] and process conditions will have to be adjusted to mitigate this effect.

The AC is typically calculated according to standard methods where the samples are placed in a furnace at a controlled temperature 550–600 °C. Several standards are available for determining the AC [22–25].¹ The AC is calculated based on the percentage of the final mass to the original dry mass.

If the residue remaining after combustion in a bomb calorimeter could be used to estimate the AC in a sample, it would provide additional valuable information without significant extra effort when a bomb calorimeter is used for HHV estimation. Overall, this would save time and resources. Typically, determination of AC is time and relatively energy intensive as heating and cooling of the sample take several hours [26]. This would make the calorimeter much more attractive compared to an elemental analyzer in combination with mathematical models for HHV determination in terms of time, cost and information content. Surprisingly, this has not been considered in waste-to-energy applications.

Previously, the residues from a bomb calorimeter have used to determine the AC of biological (plant and animal) samples in the context of ecological studies [27–29]. Núñez-Reguira et al., (2001), reported AC based on bomb calorimetry for forest waste biomass [29]. However, they did not investigate how these values correlate to ash content determined by a standard method using furnace ignition. Cummins (1967) compiled AC from bomb calorimetry for a wide variety of biological samples but did not compare it with standard ashing experiments, though it was acknowledged that the calorimeter ash will be different from furnace ignition values [28]. Sisula and Vertanen (1977) found significant differences in AC between bomb calorimeter residue and muffle furnace ashing of snail samples with the former underestimating AC [30]. Reiners and Reiners (1972) also found that calorimetry underestimated the ash content for a number of plant materials [27]. They built linear regression models, which correlated well with furnace-based ash content, though the slope and intercept values were different based on the plant material. One of the reasons for the

difference is that the bomb reaches temperatures well above 600 °C during combustion, which leads to the evaporation of inorganic salts and carbonate [31,32]. Many of these papers were concerned with vertebrates, mollusks or individual plant samples, where precision of calorific content on an ash free basis is of great importance for dietary information on small scales. None had investigated garden waste from a municipal facility for the purposes of bioenergy research, where small discrepancies in AC are tolerated up to 10% [22,24]. It is possible that, due to the nature of the tests, material placed in a bomb calorimeter could have a higher level of oxidation and thus the residue could have higher mass than from a furnace; or the bomb could expel more volatiles such as chlorine and thus have a lower mass.

To the best of our knowledge, the residue comparison between furnace ash content and bomb calorimeter tests for domestic garden waste has never been explicitly carried out, though the assumption of equivalency has been made in research [33]. In this work, we rigorously investigate the potential for using the bomb calorimeter residue to determine AC of green waste from two distinct geographical regions in Australia by comparing AC obtained by following two different standards, EPA 1684:2001 and ISO 18122:2015.

2. Methodology

Green waste samples were collected over a yearlong period from two waste management facilities in Australia, one in a tropical climate (near Darwin) and the other in a desert (near Alice Springs). The source of the green waste was domestic garden waste that residents brought to the sites and was kept segregated from the rest of the landfill. The waste was then mulched and left in piles; water is added to promote the growth of anaerobic bacteria to heat the piles to a temperature of a minimum 60 °C and a duration of at least three days to destroy any seeds that may be present. It was at the completion of this stage that the samples were collected.

The actual constituent species of plants that make up the waste was unknown because it was dependent on what people brought in from their yards. It is expected that the materials would vary between locations based on the differing climates. It is known, from the garden waste management companies, that the vast majority of the tropical waste was generally from various palm trees, whereas the waste in the desert had no palm tree waste since that was separated out. Overall, waste from both locations was mainly lignocellulosic material.

Waste from Alice Springs was collected in 1 L airtight plastic bottles and shipped to Darwin for testing throughout a year. Darwin samples were collected in resealable plastic bags and driven back to the laboratory. The samples were dried in an oven at 105 ± 2 °C on arrival to the lab (within 30 min) to determine the moisture content. Once all moisture was removed, as determined by constant mass, each sample was blended until the particle sizes were less than the openings in a 1 mm sieve. Large woody pieces and rocks were removed before blending so as not to damage the equipment. This powdered form was then used for both ash tests and bomb calorimeter tests. During the blending process, the samples' moisture content increased and so they had to be dried again before all subsequent measurements.

2.1. Elemental (CHNSO) analysis and HHV calculations

The elemental composition of the garden waste samples was determined via an organic elemental analyzer (ThermoFisher Flashsmart). For CHNS analysis, ~3 mg of sample was put into a tin capsule with 8–10 mg of the combustion aid, vanadium pentoxide. For O analysis, ~1 mg of sample was placed in a silver capsule. All tests were run in triplicate and averaged. Results from the EPA AC and CHNSO tests were then input into various equations from literature that were designed to calculate the HHV. In total, we compared seven models to our experimental results delineated in the results section. To determine the accuracy of each model, we calculated the mean absolute error (MAE) and

¹ The EPA report [EPA] refers to the test as measurement of fixed solids, however there is some amount of variation in terminology. Consensus in the bioenergy field seems to refer to ash content as the remaining mass after oxidation at ~550 °C.

mean bias error (MBE) according to the Eqs (1) and (2):

$$MAE = \frac{1}{N} \sum_{i=1}^N \left| \frac{HHV_i^{model} - HHV_i^{experimental}}{HHV_i^{experimental}} \right| \times 100\% \quad (1)$$

$$MBE = \frac{1}{N} \sum_{i=1}^N \frac{HHV_i^{model} - HHV_i^{experimental}}{HHV_i^{experimental}} \times 100\%. \quad (2)$$

The experimental value is taken as the actual HHV and the MAE gives the absolute error in each of the predictive models, while the sign of the MBE shows the bias of the modelled equations.

Following the comparisons to the existing predictive models, we used multiple linear regression analysis to determine if we could find an equation better suited to our sample types. The fit was conducted using the statsmodels module in Python [34], with the measured HHV treated as the independent variable and the weight percentages of C, H, N, S, O and the ash content as independent variables according to Eq (3):

$$HHV = c_1[C] + c_2[H] + c_3[N] + c_4[S] + c_5[O] + c_6[ash]. \quad (3)$$

After the fitting procedure was completed with all the variables included, if any coefficients had p-values greater than 0.05, they were deemed to be insignificant, and the fitting procedure was rerun with only the significant coefficients to determine the final equation. A second fitting procedure was conducted using only the AC, since that has been shown to be an accurate calculation [5] and would be based on the simplest laboratory measurement performed.

2.2. Furnace ashing

Two standard methods for measuring ash content were considered: EPA Method 1684 and ISO 18122:205 standard for AC solid biofuels. All samples were measured using the EPA method since it is the easiest procedure to follow as it only requires a basic furnace. Due to the more stringent requirements of the ISO procedure, only a subset of samples from each location was used because of equipment availability.

2.2.1. AC using EPA method 1684

Porcelain crucibles were filled with approximately 15 g of dried sample. Each sample was run in triplicate simultaneously. The crucibles were loaded together into a muffle furnace (Hareus M110) at room temperature and heated to 550 °C for a minimum of two hours (ramp time ~ 50 min). The crucibles were removed and placed in a desiccator to cool to ambient temperature. The samples were then weighed, and the process repeated until they reached constant mass. Our particular samples required multiple furnace cycles, usually at least three and up to seven. The ash content was determined on a dry weight basis according to Eq (4):

$$ash\ content = \frac{mass\ of\ ash}{mass\ of\ dry\ sample} \times 100\%. \quad (4)$$

2.2.2. AC using ISO 18122:2015

In order to follow the stricter requirements of the ISO procedure, a different furnace was used than for the EPA procedure. For this test we used a highly controllable, uniform tube furnace (Carbolite-Gero EHA) with the ends open and placed in a fume cupboard to allow for sufficient airflow. Sample sizes of approximately 3 g of powder were used for these tests to meet the sample loading requirements of the standard. Each sample was run individually with consecutive duplicates, while allowing the furnace to achieve room temperature between runs.

2.3. Bomb calorimeter ashing and HHV measurements

An oxygen bomb calorimeter (IKA C5000) was used in isoperibolic mode to determine the calorific content of various samples. Samples were placed in a bomb vessel and pressurized to 30 bar of UHP oxygen.

The sample was then ignited by a cotton thread connected between an ignition wire and the sample. As a consequence of the calorific test, residual mass of the sample was left behind. We compared the residual mass as a percentage of the initial dry mass, similar to Eq. (4) with the furnace.

The sample in powdered form had to be pelletized before combustion in the bomb, otherwise it could burn in an explosive manner. A one-ton arbor press and a custom die were used to compress the powder into pellets. The pellets were found to be much more tightly bound if a small amount of distilled water was added to make a paste with the powder before pressing. As this added moisture to the samples, the pellets were dried in an oven at 105 °C until constant mass was achieved (at least overnight) to return them to their dried state.

The pellets (~0.3–1.0 g) were placed into a quartz crucible within the bomb for combustion. It was observed that when the pellets were inserted, small particles would be drawn from the main pellet and adhered to the crucible wall through electrostatic attraction. As the smaller particles were no longer in contact with the pellet, complete combustion of all the sample could not be assured. Contrarily, the cotton thread was seen to be electrostatically repelled by the crucible, so care had to be taken to ensure good sample contact to achieve ignition. On occasion, the pellets were also found to explode leaving unburnt sample that affect the accuracy of the calorimetry test. The solution to all these problems was to add a small amount (~0.5 g) of oil as suggested by the calorimeter manufacturer.

The pellet was placed into the bottom of the crucible. A dropper was used to add canola oil around the crucible wall where it formed a film around the edges and flowed toward the bottom. The pellet soaked up the excess oil. Once the cotton thread contacted the oil, good contact between all of the sample and the thread was made. The heating value was corrected for the sample to take into account the oil, but no measurable ash (less than 0.1 mg) was left due to the oil or cotton thread. The mass of residue was used as the mass of ash in Eq. (4) to calculate the ash content. Tests were run in consecutive triplicate and averages calculated. Statistical analysis of the results was completed using custom Python code and the NumPy library; graphs were generated using the matplotlib library. Statistical significance was evaluated at 95% confidence ($\alpha = 0.05$).

3. Results

3.1. HHV calculations from CHNSO and ash results

The MAE and MBE were calculated using measured values of carbon, hydrogen, nitrogen, sulfur, oxygen and ash content as inputs to select predictive models from literature that have these variables as inputs, whose results are shown in Table 1. The fits to our Alice Springs data had R-squared values of 0.95 and 0.91 for No. 8 and No. 9, respectively. The only coefficient with statistical significance for Darwin samples was the AC, as seen in No. 10, which had an R-squared value of 0.92.

The predictive models taken from literature did not show a good agreement with our experimental values. With the exception of No. 1 of the equations, the models had a tendency to overestimate the true HHV value. Not surprisingly, our bespoke fits showed the best results. However, even with high R-squared values, for single data points there were differences between experimental and calculated results as high as 15% for Darwin and 20% for Alice Springs.

Further investigations were carried out to determine the organic makeup of the waste. In Fig. 1, a van Krevelen diagram shows the relationship between hydrogen/carbon and oxygen/carbon ratios, which are related to the HHV [37]. A quarter of the Darwin samples were outside the normal region for biomass. This could have been caused by some sort of hydrocarbon contamination such as plastics or petrochemicals (e.g., pesticides or fuels used in gardening equipment), which would raise the hydrogen content. Except for one, the samples for Alice Springs were within the standard biomass region.

Table 1

Calculations of the MAE and MBE of the predicted HHV from equations based on carbon, hydrogen, nitrogen, sulfur, oxygen and ash content for samples collected from Alice Springs and Darwin. Nos. 8 and 9 are based on Alice Springs values and No. 10 is based on Darwin values.

No.	HHV equation (MJ/kg)	MAE (%) (Alice Springs)	MBE (%) (Alice Springs)	MAE (%) (Darwin)	MBE (%) (Darwin)	Ref.
1	$19.914 - 0.2324 \times Ash$	9.36	-8.66	8.82	-8.46	[5]
2	$0.3259 \times C + 3.4597$	16.50	16.50	17.02	17.02	[5]
3	$-1.3675 + 0.3137 \times C + 0.7009 \times H + 0.0318 \times O^*$	8.74	5.68	7.53	2.42	[5]
4	$(3.55 \times C^2 - 232 \times C - 2,230 \times H + 51.2 \times C \times H + 131 \times N + 20,600)/1,000$	18.51	18.51	26.48	26.48	[35]
5	$0.3491 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times Ash$	10.75	8.17	10.40	5.55	[36]
6	$0.2949 \times C - 0.8250 \times H$	9.93	8.51	9.15	6.24	[8]
7	$-0.8738 \times N \times H^{-1.3101} - 0.1583 \times C \times O^{0.3497} + 0.3856 \times C \times (H \times O)^{0.1462} + 2.1436 \times (\frac{H}{O})^{-0.3846} + 1.076 \times C \times H^{-0.3846} + 0.1098 \times N \times S - 11.2794 \times (\frac{H}{C})$	14.96	14.88	13.84	13.34	[16]
8	$25.1690 - 0.5191 \times C + 3.6846 \times H - 0.2426 \times Ash$	2.95	0.22			This work
9	$20.9684 - 0.2274 \times Ash$	4.16	0.34			This work
10	$20.2271 - 0.2142 \times Ash$			4.35	0.29	This work

$O^* = 100 - C - H - Ash.$

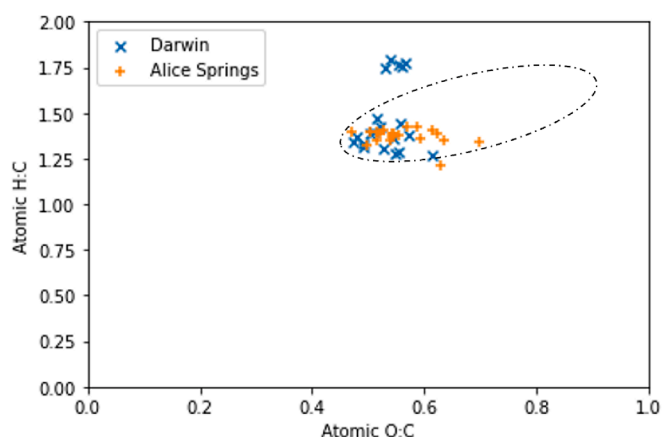


Fig. 1. A Van Krevelen diagram of the waste based on the results of elemental analysis. The area enclosed by the outline is typical for biomass.

3.2. Ash content comparisons between furnace and bomb calorimeter

3.2.1. Alice springs

In total, 20 samples from Alice Springs were used to conduct the EPA ash method and the bomb calorimeter test. The AC ranged from 12 to 50%. The mean of three runs per sample in each test method were used for comparison. A paired *t*-test was run between the means for each sample by the two methods and it was found the difference between them was statistically significant ($p = 0.001$). The EPA results tended to be slightly higher than the bomb results, by an average of 2.8% based on the difference between the test methods on a per sample basis.

The dispersion of each method was investigated by comparing the standard deviation of the three runs across the range of ash contents. Previous researchers had found that the variance of the measured ash increased as the ash content increased [27]. A plot of the standard deviation of the sample means based on the furnace method and on the calorimeter method is shown in Fig. 2. A linear regression of the plots showed no correlation between standard deviation and percentage of ash in either test, which both had p -values of ≥ 0.3 and R -squared values of ≤ 0.1 .

As there was no clear sign that the ash content SD depends on the

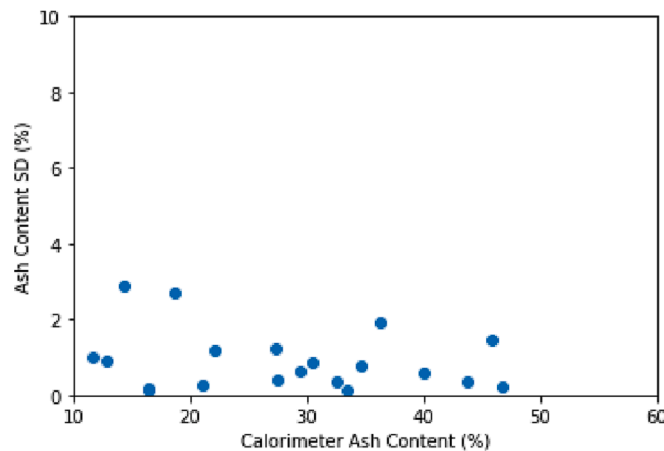
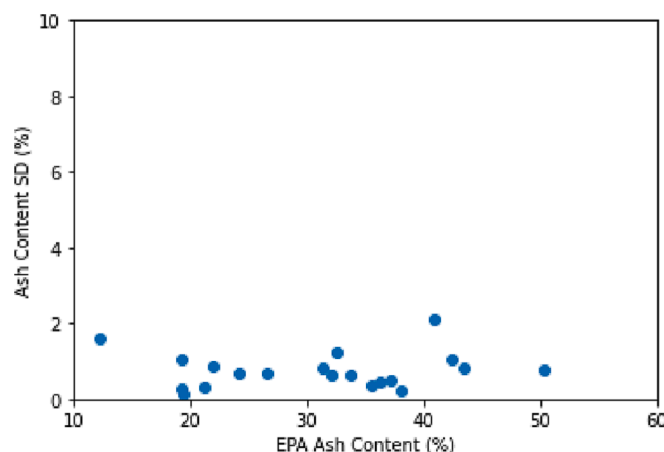


Fig. 2. Plots of the standard deviation of ash content versus the ash content of Alice Springs samples. Top: ash content from the furnace. Bottom: ash content from the bomb calorimeter.

amount of ash, it was assumed that variance remained constant for all ash values and a pooled-SD was calculated to quantify, in a more statistically valuable way, the dispersion of the methods. With all the samples taken as an ensemble, the furnace method had a mean of 30.9% and a pooled-SD of 0.9%; the calorimeter method had a mean of 28.1% and pooled-SD of 1.2%.

A comparison of the two test methods is in Fig. 3, where the AC found through ignition in the bomb is seen versus the AC from the furnace. A linear best fit line had an R-squared value of 0.92, indicating a strong linear relationship. The values of the fit can be seen in Table 2. The slope is near unity. The y-intercept had a value of -4.79, showing a bias to underestimate the AC using a bomb calorimeter versus a furnace, but does not reach statistical significance with $p = 0.07$.

From the Alice Springs samples, a subset of five samples were run using the ISO method as a comparison to another standard. The samples were chosen to cover the range of ash content results here, from ~10–50%, in increments of roughly 10%. The results are shown in Fig. 4 with the values for linear regression models in Table 3. The R-squared values were 0.97 and 0.84 for the EPA and calorimeter methods, respectively. The largest difference in AC between any samples was 9.7%, which is between the ISO measurement and calorimeter measurement at the second to highest AC data point. All three methods agree with each other within statistical significance.

3.2.2. Darwin

Similar comparisons were made between the muffle furnace ash method and the bomb calorimeter method for 20 Darwin samples. AC ranged from 25 to 56%. A paired t-test between the means show that the results were not significantly different between the two methods ($p = 0.7$).

The dispersions were also estimated for this data set to see if the material had an impact on the standard deviation when compared to ash content. The results are shown in Fig. 5; linear regression on the plot both resulted in R-squared values of less than 0.3, showing a poor linear fit between SD of ash versus the amount of ash. The p-value for calorimeter fit was 0.6, showing no significant trend in SD. While the p-value for the slope of the EPA fit was statistically significant with $p = 2 \times 10^{-10}$, the value of the slope was only 0.09 and deemed low enough to ignore over the range measured. Therefore, the pooled SD was calculated and was found to be 2.3% for both methods.

The ash content from the EPA test and the calorimeter are compared in Fig. 6. A linear regression returned an R-squared value of 0.90, demonstrating a strong relationship between the methods. The values of the fit can be found in Table 4. The slope is within one standard error of

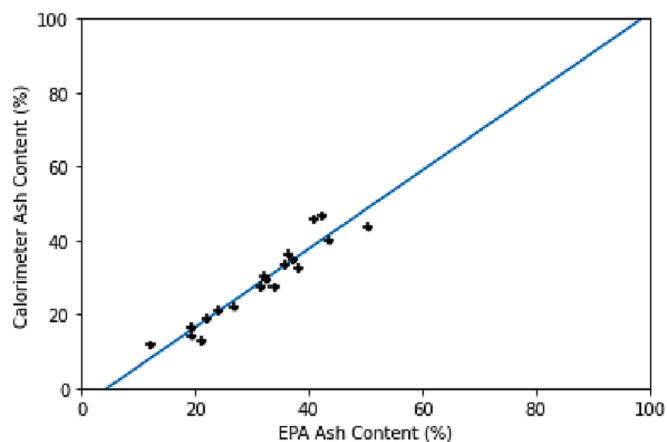


Fig. 3. Scatter plot of the calorimeter ash content versus the ash content from the furnace for samples from Alice Springs with error bars equal to the pooled standard deviation of each method. The solid line is the line of best fit from linear regression whose values are seen in Table 2.

Table 2
The linear regression values from Fig. 3.

	Value	Standard error	t-value	p-value
Intercept	-4.79	2.44	-1.97	0.07
Slope	1.07	0.08	14.15	3×10^{-11}

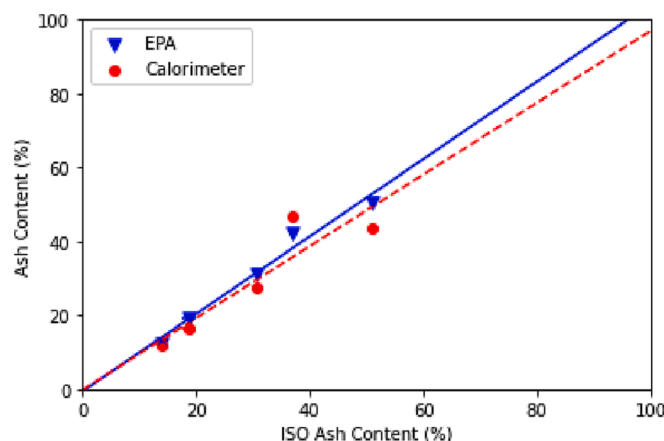


Fig. 4. Scatter plot of EPA ash content and calorimeter ash content versus the ash content of the ISO ash content test for Alice Springs samples. The y-error bars are the pooled standard deviations of the methods; the x-error bars are cover the range of the two individual measurements. Error bars that cannot be seen are smaller than the data points. The lines are lines of best fit from linear regression whose parameters are given in Table 3.

Table 3
The linear regression values from Fig. 4.

EPA ash content test				
	Value	Standard error	t-value	p-value
Intercept	-0.60	3.27	-0.18	0.87
Slope	1.05	0.10	10.60	0.002
Bomb calorimeter ash content test				
Intercept	-0.19	8.13	-0.02	0.98
Slope	0.97	0.25	3.95	0.03

unity, indicating that the slope is not significantly different from unity. The intercept is also within the standard error of the origin.

A subset of five of the Darwin samples were run using the ISO method for comparison. The samples from Darwin had ash contents with less spread than Alice Springs, but as wide a range as possible was taken covering a range ~26–54%. The results are shown in Fig. 7 with the fit parameters from linear regression models in Table 5. The R-squared values for the EPA and calorimeter methods were 0.97 and 0.84, respectively. The largest difference in AC between any of the measurements for a single sample was 8.0% between the calorimeter and ISO methods at AC around 55%. All three methods for measuring AC were in agreement to within statistical difference.

4. Discussion

The models from literature were unable to accurately predict HHV values based on elemental and ash contents for both Alice Springs and Darwin locations. This is likely due to the need to derive these formulae for a particular biomass system [10]. One reason the models were so poor at predicted the HHV for our samples was that our AC was much higher than is normally seen in biomass. Three of the equations (No 2, 4 and 7) did not contain ash terms and were also those that were the worst at predicting the HHV.

From our regression models of our data, we found that AC had the

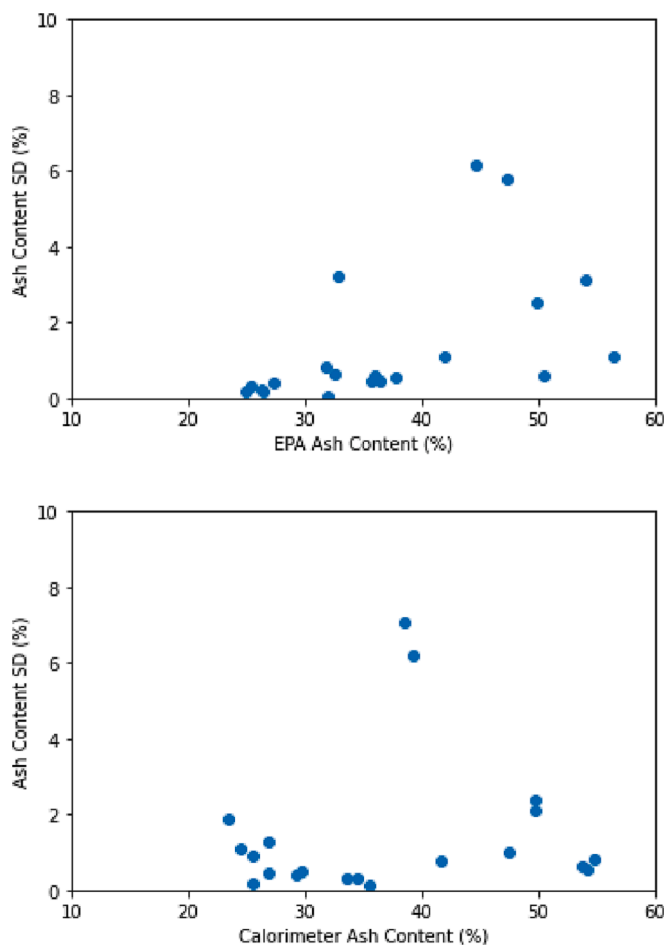


Fig. 5. Plots of the standard deviation of ash content versus the ash content of Darwin samples. Top: ash content from the furnace. Bottom: ash content from the bomb calorimeter.

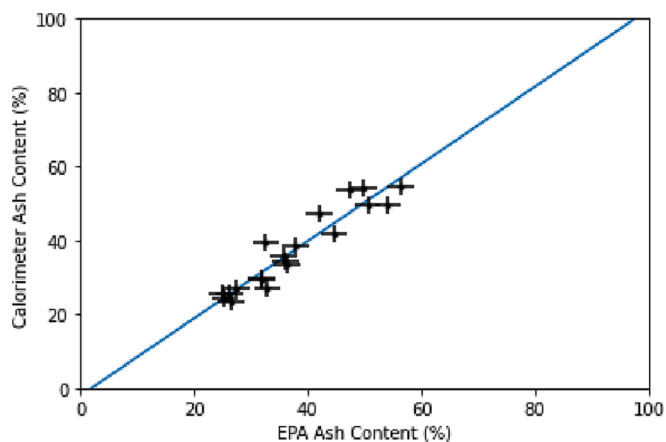


Fig. 6. Scatter plot of the calorimeter ash content versus the ash content from the furnace for samples from Darwin with error bars equal to the pooled standard deviation of each method. The solid line is the line of best fit from linear regression whose values are seen in Table 4.

largest impact on the HHV out of the studied parameters, with intercepts and coefficients similar to No. 1. However, even our bespoke models for our data, which had R-squared values above 0.9, were off by up to 20% for single data points. A difference this large could have detrimental impacts on an operational bioenergy facility if planning were based on

Table 4
The linear regression values from Fig. 6.

	Value	Standard Error	t-value	p-value
Intercept	-2.01	3.2	-0.63	0.54
Slope	1.05	0.08	12.73	2×10^{-10}

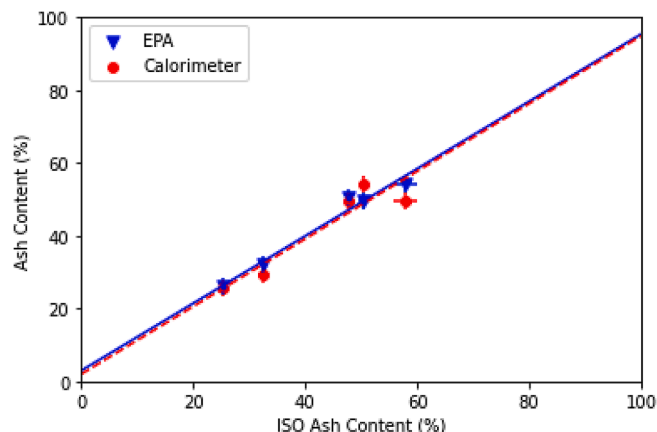


Fig. 7. Scatter plot of EPA ash content and calorimeter ash content versus the ash content of the ISO ash content test for Darwin samples. The y-error bars are the pooled standard deviations of the methods; the x-error bars cover the range of the two individual measurements. Error bars that cannot be seen are smaller than the data points. The lines are lines of best fit from linear regression whose parameters are given in Table 5.

Table 5
The linear regression values from Fig. 7.

EPA ash content test				
	Value	Standard error	t-value	p-value
Intercept	2.94	4.05	0.73	0.52
Slope	0.93	0.09	10.13	0.002
Bomb calorimeter ash content test				
Intercept	1.98	8.85	0.22	0.84
Slope	0.93	0.20	4.67	0.02

HHV calculations from this predictive model. Given the everchanging composition of domestic garden waste it does not seem likely that a single expression would be found that can accurately predict the HHV value from elemental and ash contents. The high levels of AC in our samples would likely exclude them from being used as a biofuel feedstock but could potentially still be used for energy through incineration, especially if mixed with a lower AC waste. The ash disposal costs would not be expected to be too high if the energy plant was co-located on the waste site.

As seen above, the need for direct measurement of HHV for mixed garden waste could not be avoided when accuracy was important. However, we found that a test singularly to determine AC was not needed as the residue from bomb calorimetry was highly accurate.

The *t*-test comparing the furnace and calorimeter method results showed a statistical difference between the methods for Alice Springs samples, however the linear regression analysis did not show a significant difference. Even though the *t*-test indicated a statistically significant difference, the actual differences were still within the 10% range that is considered acceptable by the EPA and ISO standards. There was no statistical difference between the tests from the Darwin samples. Future experiments are planned to determine the elemental composition of the ash residues from the various samples.

There was a small bias of calorimeter tests to produce lower AC, as was mentioned by previous works [27–30,32], however our results were

still within the acceptable limits of variation (10%) according to the standard AC tests. From this, we can rule out higher oxidation levels in the bomb since the ash had lower mass. The slightly lower mass could have been due to higher volatilization, but we believe the reason this difference was still acceptable was that our samples did not contain large amounts of inorganic salts, at least compared to the total amount of ash. Reiners and Reiners found that organic solids with higher ash (16–54%) had similar AC values for furnace ignition and bomb calorimetry [27].

5. Conclusions

Based on the results above, it was found that models to predict the HHV of mixed garden waste from elemental analysis and AC, though statistically within reason, could not be relied upon to always be accurate. Direct measurement through bomb calorimetry should therefore be the preferred method for mixed green waste where biomass and contaminant energy content can vary significantly. Additionally, the residue from the test could be used to eliminate the necessity of laboratory tests carried out exclusively to determine AC as differences between values from those methods and the residue were always below 10 %. In fact, the difference between the values from the two standard AC determination methods were similar to the differences between the AC using the residue and these methods over a large range. The variance between duplicates for all tests was quite small with a standard deviation no more than 2.5 %. Due to the complete combustion on the initial firing of the bomb calorimeter, there is no need to reignite the ash, saving valuable time and resources since determination of AC on its own is both time and relatively energy intensive. The residue is a model-free approach to measure AC as the residue directly translates to the AC. These findings were true for the two drastically different climate zones of Alice Springs and Darwin samples throughout the seasons of a year,

Appendix

A1. Measured characteristics of garden waste feedstock from Alice Springs municipal waste facility and used to calculate the values in Table 1. All values are based on a dry basis with percentages referring to wt%. Ash values presented were those measured by EPA Method 1684.

Sample	Ash(%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)	HHV (MJ/kg)
1	31.4	37.3	4.2	0.8	0.1	31.5	14.3
2	38.1	33.6	3.8	0.9	0.1	26.6	13.1
3	12.2	46.0	5.5	0.5	0.1	36.0	17.3
4	26.7	45.5	5.3	0.7	0.1	28.4	15.6
5	42.3	41.1	4.7	0.8	0.1	34.1	10.3
6	33.8	35.6	4.1	0.9	0.1	25.7	14.3
7	32.6	32.9	3.8	0.7	0.1	24.4	13.9
8	36.3	32.1	3.5	0.7	0.1	21.3	12.6
9	32.1	36.4	4.1	0.8	0.1	24.9	13.7
10	19.3	42.7	5.0	0.9	0.1	30.1	16.9
11	19.3	42.7	5.0	0.8	0.2	34.9	16.5
12	21.9	43.9	5.1	0.8	0.0	29.5	15.7
13	21.2	42.8	5.1	0.7	0.1	32.5	16.9
14	19.4	46.7	5.4	0.5	0.0	32.4	16.3
15	37.1	32.4	3.7	0.6	0.1	23.3	12.3
16	24.1	43.1	5.0	0.7	0.1	31.3	15.2
17	50.4	26.7	3.0	0.7	0.1	24.9	10.0
18	40.9	34.6	3.5	0.9	0.2	29.0	9.7
19	35.6	37.9	4.4	0.7	0.0	26.0	12.6
20	43.4	34.2	4.0	0.9	0.1	24.6	11.5

A2. Measured characteristics of garden waste feedstock from Darwin municipal waste facility and used to calculate the values in Table 1. All values are based on a dry basis with percentages referring to wt%. Ash values presented were those measured by EPA Method 1684.

indicating a broad application. Thus, this study indicates that the AC measured using the residue of the bomb calorimeter can be used in place of the standards thereby significantly reducing the time and cost of the tests whilst getting more accurate results for HHV through direct and model-free measurement compared to the models suggested in the literature.

CRedit authorship contribution statement

Jeremy B. Trombley: . **Chun Wang**: Data curation, Investigation, Writing – review & editing. **Suresh N. Thennadil**: Formal analysis, Funding acquisition, Investigation, Methodology, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Sample	Ash(%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur(%)	Oxygen (%)	HHV (MJ/kg)
1	35.8	33.5	4.9	1.1	0.1	25.3	12.6
2	37.8	32.0	4.7	1.2	0.1	23.9	12.6
3	32.5	37.4	5.6	1.2	0.0	26.8	12.1
4	26.5	37.0	4.0	1.0	0.1	27.4	14.8
5	24.9	38.2	4.4	0.8	0.0	25.6	14.8
6	26.2	37.4	5.4	1.2	0.0	26.3	14.5
7	27.3	37.4	5.5	1.1	0.0	27.6	14.1
8	31.9	34.9	4.0	1.1	0.1	26.7	13.7
9	31.9	33.5	4.0	1.0	0.1	24.9	13.8
10	25.4	37.4	4.3	0.8	0.1	25.4	14.8
11	36.0	33.4	3.9	0.9	0.1	23.1	12.7
12	50.5	26.2	3.2	0.8	0.0	17.9	9.5
13	32.8	36.0	4.0	1.2	0.1	23.5	14.1
14	36.4	33.3	3.8	1.0	0.0	21.2	12.7
15	47.3	22.8	2.6	0.9	0.0	16.5	8.8
16	56.4	29.5	3.2	1.1	0.0	19.3	8.7
17	44.6	24.6	2.6	1.1	0.0	18.0	11.4
18	49.8	29.3	3.3	0.8	0.0	18.6	8.8
19	54.1	24.4	2.6	0.7	0.0	19.9	9.3
20	42.0	30.4	3.3	0.8	0.0	21.3	10.2

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