Improved Metrological Methodology to Address the Challenges Associated with the Determination of Biofuels Calorific Value by Bomb Calorimeter

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The challenges associated with biofuel quality come from its heterogenous nature as biomass crops grow in different lands and under different conditions. Moreover, the inconsistency of the handling and sampling techniques in the laboratories or in the feedstock storage piles increase biomass variability. These issues affect the calorific value and as a result, the accuracy of the measurement for each feedstock pile of the measured data might be widely scattered. Furthermore, the current standards, e.g., ISO, DIN or ASTM are limited and do not consider the deviations caused by determination errors during the measurements. Therefore, this study quantifies the causes of these deviations by performing an inter-laboratory comparison on a metrological level between 3 national metrology institutes. Eventually this comparison helps to optimize the existing strategies and provides an enhanced technical practice for the determination of the calorific value by bomb calorimetry. It has been found that by assuring that the equilibrium moisture content of the samples is reached and that by avoiding the sources of error during the measurements, the repeatability of the samples can be improved by up to 50%. Consequently, this improvement will help to lower the final uncertainty by 10–25%.

1. Introduction

One of the main causes of the global warming is the excessive use of fossil fuels, which emit when combusted substantial amounts of CO_2 into the atmosphere. Out of the many possible renewable energy alternatives, biomass/biofuels feedstock is expected to play a major role in the next decades. By 2030 the EU commission aims to increase the use of biomass to represent 60% share of the renewable energy consumption (Irena, 2014). To achieve this goal and to allow for fair pricing between the biomass provider and the end user, the challenges that are associated with biofuel quality would need to be studied and resolved. The long-term reliability and global comparability of biofuels analytical data must be guaranteed, and full knowledge of the measurement chain is required to enable traceability to the International System of Units (SI) for field analyses of both liquid and solid biofuels. That's where the determination of the caloric value of the biofuels is an important aspect to determine its suitability in a particular industry. Moreover, the calorific value is one of the main quality control criteria which reflects the performance of the fuel. However, the repeatability of the measurements of biofuels calorific value tends to show a wide scattering during the sample measurements (Pedišius et al., 2021). Moreover, it is hard to reproduce the same results in different laboratories due to heterogenous nature of biomass and the determination errors. Furthermore, the current techniques for the determination of the calorific value of biofuels which rely on calorimetric technique show poor results in intercomparison between different laboratories. This study aims on the improvement of the calorimetric practice to ensure better repeatability and reproducibility. The repeatability refers to the standard deviation of several measurements performed by the same operator under specific conditions, while reproducibility is the ability to obtain the same results but

performed in another laboratory and by different operator under the same experimental conditions (JCGM, 2008). The improvement in repeatability and reproducibility will have a significant impact from an economical point of view If the biomass is purchased based on its calorific value (Gendek et al., 2018) and calculated on dry basis (Atkins et al., 2016). Therefore, if there is wide scattering and high uncertainty in the measured calorific value, financial lose maybe expected. This financial loss will affect the biomass supplier or the end user such as power plants. Typically, wood chips and wood pellets are the most common form of biomass used as raw fuel (Erik et al., 2021). Therefore, an interlaboratory comparison between 3 metrology institutes (PTB, TUBITAK, BRML) was performed by testing two different types of wood chips. The goal of this paper is to provide an improved technical practice to improve biofuels repeatability and reproducibility in calorific value measurements. The final overarching of this research will support the transition into a clean CO_2 neutral energy alternative where biofuels have a crucial role to secure the stability of the future energy supply.

2. Materials and methods

The design of the comparison consists of two different test cycles using high-quality (WC-HQ) and industrial quality (WC-IQ) wood chips. Since biomass particle size is crucial in biomass combustion and conversion (Krátký et al., 2021), the samples were grinded by the institutes to around 1 mm. In the first cycle, the samples were analyzed following the international standard EN ISO 18125:2017. Ten measurements for each sample are performed by the metrology institutes to compare the repeatability and reproducibility of the results. In cycle 2 the samples were retested using an improved practice, which is based on the experimental findings from cycle 1. Specifically, it relies on a well-mixed homogenized sample prepared by only one institute and takes into consideration the variations caused by the sample heterogeneity, operator's sampling and handling techniques. In both cycles, all instrumental setups consist of isoperibol bomb calorimeters that were calibrated using a mass from reference benzoic acid causes an equivalent temperature rise that would result from the sample mass in (g). The main operating concept of a bomb calorimeter is based on charging a known mass of the sample inside a closed vessel (bomb) filled by pure oxygen at around 30 bar. This bomb vessel is connected with electrodes and surrounded by a water bucket. When the sample burns the temperature inside the bomb increases and as a consequence the temperature of the water outside the bomb increases due to the heat transfer from the bomb to the water. The temperature values are recorded. At the end of the experiment the liquid residual inside the bomb is rinsed by distilled water and collected for further analysis by ion chromatography (IC) or titration. The cause of the analysis is to determine the amount of inorganic anions of NO_3^- and SO_4^{2-} in the liquid which are used for necessary thermochemical corrections. The anions reflect the presence of their respective acids inside the vessel, HNO_3 and H_2SO_4. These acids contribute to the final temperature rise, which consequently influences the calorific value of the samples (Jessup, 1960). Table 1 summarizes the used types of calorimeters as well as the instruments for residual analysis for each institute within the comparison.

Table 1: Instruments used for the calorific value determination

Institute	Calorimeter type	Residual analysis instrument
PTB	Isoperibol oxygen bomb calorimeter Parr 6200	Ion chromatography – Metrohm IC 761
BRML	Isoperibol oxygen bomb calorimeter Parr 6200	Titration using barium hydroxide and hydrochloric acid
TUBITAK	Isoperibol oxygen bomb LECOAC600	Assumed from ISO18125:2017 / Ion chromatography – Dionex ICS3000

The determination of the heat capacity and the calorific value is based on the Regnault Pfaundler equations given in ISO 18125 (2017) as shown in equation 1 and 2 respectively.

$$\varepsilon = \frac{m_{ba} \times q_{v,ba} + Q_{fuse} + Q_{ign} + Q_N}{\theta} \qquad (1)$$

where m_{ba} is the mass, in g, of benzoic acid, $q_{V,ba}$ is the certified gross calorific value in J/g, of benzoic acid, Q_{fuse} contribution from combustion of the fuse, Q_{ign} contribution from oxidation of the ignition wire, Q_N contribution from formation of nitric acid all in unit J. While θ is the corrected temperature rise, in K or in an arbitrary unit

$$Q_{v,gr} = \frac{\varepsilon_n \times \theta - (Q_{fuse} + Q_{ign} + Q_N + Q_S)}{m_1} \qquad (2)$$

where $Q_{V,gr}$ is the gross calorific on wet basis of the fuel, in J/g and m_1 is the mass of the fuel, in g.

3. Results

Figure 1 shows the scattering of the obtained calorific values on wet basis (as per determined basis) for cycle 1 and cycle 2 and for both samples of wood chips, high and industrial quality. This scattering is defined as the reproducibility difference between the institutes. This difference is between the maximum calorific value and the minimum calorific value out of the comparison results. For cycle 1 a larger scattering can be observed than for cycle 2, i.e., 800 J for cycle 1 and 200 J for cycle 2, respectively.
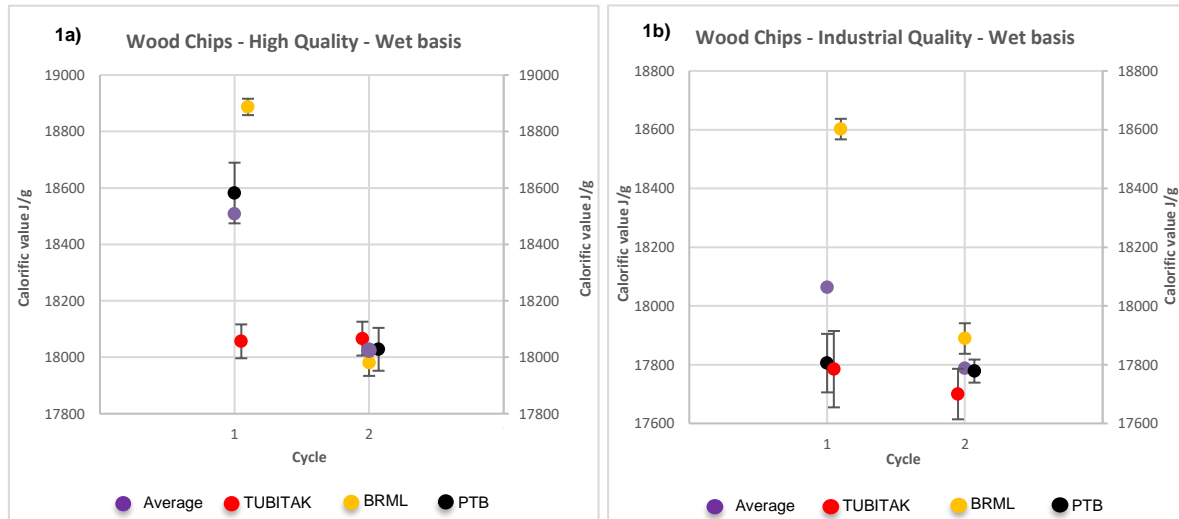

Figure 1: Comparison on wet basis of WC-HQ (Figure 1.a- left) and WC-IQ (Figure 1.b – right)

Figure. 2, shows the results of the recalculation on a dry basis after correcting for the moisture content according to the following equation:

$$Q_{v,gr,d} = q_{v,gr} \; x \; \frac{100}{100 - M_{ad}} \tag{3}$$

where $Q_{V,gr,d}$ is the gross calorific value on dry basis, in J/g and M_{ad} is the moisture content in percentage.
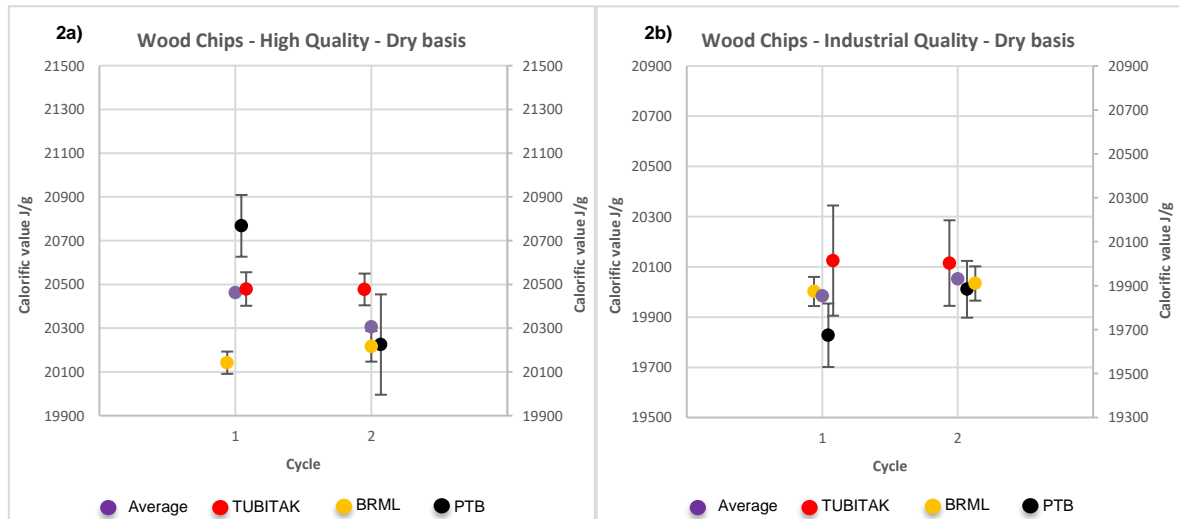

Figure 2: Comparison on dry basis of WC-HQ (Figure 2.a - left) and WC-IQ (Figure 2.b - right)

The reproducibility difference in cycle 1 has decreased to around 600 and 300 J for WC-HQ and WC-IQ, respectively. For cycle 2, the difference in case of WC-HQ increased to 260 J, while for WC-IQ it has decreased to 120 J. The theoretical expectation up front was that the difference should be lower in both cycles on the dry basis. This unexpected increase of the reproducibility difference in cycle 2 confirms the sensitivity of the moisture content determination on the final calorific value. The criteria to judge such variation is given in the ISO

18125:2017 standard, which provides an expected reproducibility for wood chips of 400 J. Therefore, by looking to cycle 1 and cycle 2 differences, it can be stated that the cycle 1 value for WC-HQ would be rejected while for cycle 2 the reproducibility differences for both samples are still better than what is expected by the ISO standard. The wide scattering in cycle 1 helps to shape a root analysis to map all possible causes and to improve the measurements repeatability and reproducibility. Figure 3 shows the different roots which are based on the different practices and instruments used in the different laboratories. Moreover, the standards do not give sufficient information to each factor but rather general criteria that do not fit with each type of biofuel. Different biofuels need different approaches to generate the best repeatability and reproducibility.
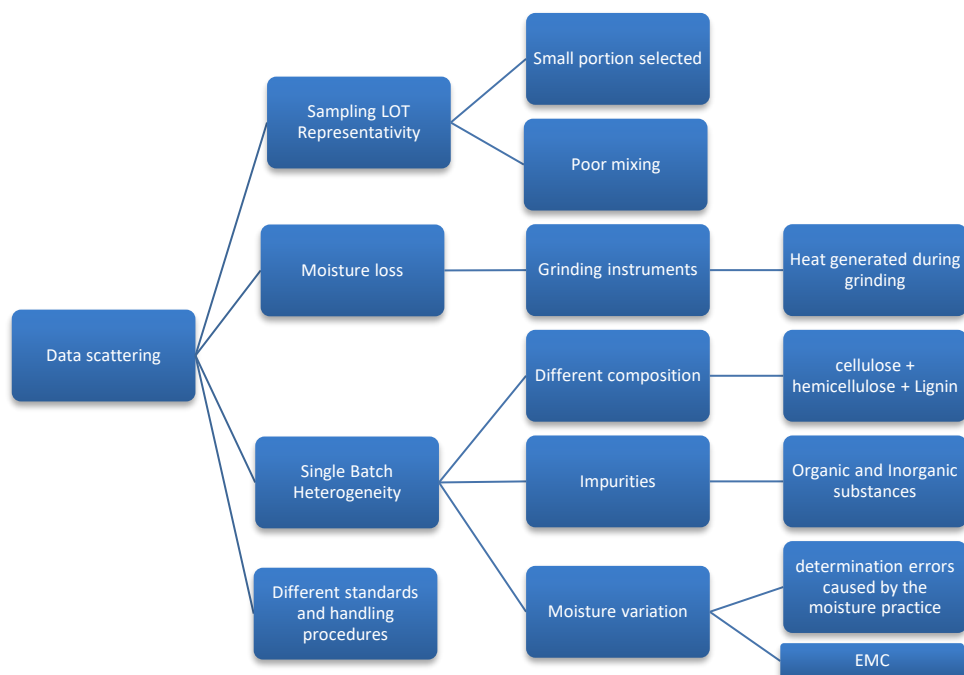
Figure 3: Root cause analysis for the data scattering

To improve the measurements in cycle 2 and to be able to quantify the impact of each factor on the final calorific value, some of these causes needed to be neutralized. The deviation caused by the sample representativity and moisture loss due to grinding has been eliminated. This is achieved by using a sample made of a larger portion of the pile (500 grams), grinded to 1mm, well-mixed and homogenized by TUBITAK UME institute. Therefore, in cycle 2 each institute had the same identical sample. Although the results have been significantly improved, there is still scattering caused by other factors such as natural sample heterogeneity, different handling procedures and moisture determination errors. Quantifying these factors is crucial to improve the repeatability of the calorific value. Table 2 shows a test performed at PTB for the sample stability over time with respect to relative humidity (RH) in the laboratory. The RH is 30% and the batch initial moisture content is around 13.2%. Moisture loss occurs over time until an equilibrium moisture content is reached, where the sample would no longer gain or lose moisture (Hoffmeyer et al. 2011). If the equilibrium moisture content (EMC) is not fully reached, weighting the sample on the balance is not stable and affects the repeatability of the calorific value since it is related to the mass. Moreover, if the sample preparation time is not fixed for all measurements and the balance resolution is less than 0.1 mg it will further influence the accuracy of the mass which impacts the calorific value and increases the scattering.

Table 2: Mass instability as a function of EMC.

EMC reached	Time (hr)	Mass (sample mass: 1.1914 g)	Moisture loss to the atmosphere in (%)
90.5%	2:30	1.1170	6.24
92.1%	4	1.1154	6.38
93.2%	5:30	1.1142	6.48
99%	24	1.1078	7.01

Improving the repeatability will lower the margin of error during the calorific value determination in each single laboratory. This improvement leads to small reproducibility difference in case of comparisons between laboratories and in particular between the biomass provider and the end-user. Consequently, this will directly contribute providing accurate cost estimations of biofuels since the possibility of deviation has been reduced.

4. Quantified and improved methodology

The ISO 14780 standard (2017) for biofuel sample preparation states that after grinding, the sample can be left up to 4 hours to reach equilibrium with temperature and moisture without naming the EMC or the obligation to do so. Based on findings from the comparison, it is urged to leave the sample reach equilibrium after grinding for 4 hours and then again before the determination of the calorific value on the day where the measurements will take place. That is because the temperature and relative humidity changes frequently and the samples need to adjust with any variation in the room conditions. The determined moisture content after equilibrium in the two phases after grinding and before analysis should not be confused with the total moisture of the sample which can be determined according to the standard ISO 18134:2 (2017). Once the sample reaches EMC its moisture no longer represents the original batch. Figure 4a shows the influence of the different cases of non-equilibrium, partial equilibrium and equilibrium moisture content on the calorific value repeatability. Different samples from a freshly prepared batch were tested in different time intervals. A Non equilibrium sample is tested directly after grinding, shows poor repeatability due to inconsistency of the moisture values. Partial equilibrium after waiting for several hours has shown better repeatability. Assuring the sample mass is stable and the EMC criteria is fully reached that is enough to assure an improvement in the repeatability by up to 50%. Such improvement in the repeatability lowers the final uncertainty of the calorific value by 10-25% depends on the calorimetric setup and the uncertainty sources considered in the calculations of the final uncertainty. On the other hand, the calorific value of the sample after reaching EMC will give higher calorific value on wet basis and vice versa. This increase in the calorific value is because of loss of moisture from the sample that goes to the atmosphere.

Moreover, to determine the sources of error during any interlaboratory comparison for biofuels, it should be based on the comparison of the calorific value on wet and dry basis. A dry basis comparison should yield less reproducibility standard deviation than on wet basis as each lab would have corrected for their respective moisture value. Therefore, any deviation on wet basis is not important as long as no remarkable scattering is observed. In case of increased scattering on dry basis that would refer to wrong results and multiple possible sources of error that needs to be further investigated. Figure 4b reveals that each institute had a slightly different moisture value which is not only due to a different EMC caused by different room conditions, but also due to errors caused during the moisture determination. Such errors depend on the type of the oven used, the heat distribution, the place of the sample inside the oven. In addition, the sample crucible and whether it provides enough surface area to dry the sample properly or not plays an important role. It is noticeable that BRML has the biggest difference in terms of moisture in cycle 1, this is because the sample is left to fully reach equilibrium for much longer time compared to the other institutes.
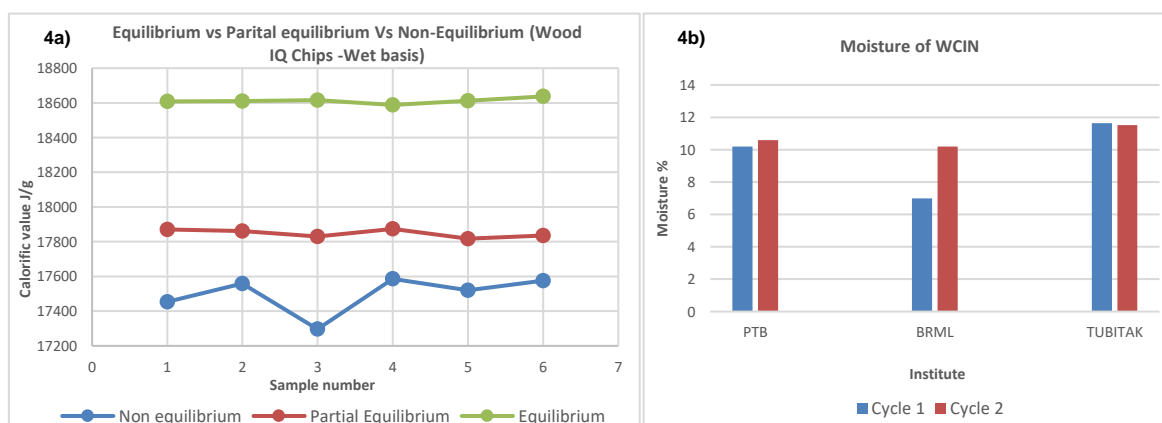

Figure 4: EMC effect on repeatability (Figure 4.a - left) and moisture values of each lab (Figure 4.b - right)

According to the root analysis, another source of calorific value deviation is caused by the operator and the different handling procedures and instruments used in each lab. This deviation is estimated to be around 20 J and was validated after testing several samples of liquid biofuels which is more stable and easier to burn. Another deviation is caused while performing the thermochemical corrections to determine the Q_N and Q_S. In practice most of the industrial laboratories are using fixed corrections based on the appendix available in the

ISO or ASTM standards (Parr instruments, 2010). These corrections do not explain the difference in case of flushing or not-flushing the bomb vessel by oxygen before the experiment to replace the air inside. The standard corrections do not consider the amount of air trapped in case of different bomb size and volume. These factors would change the results of the correction. As known in equation 2, the corrections are crucial for the final calorific value. Therefore, a wrong estimation of the corrections would cause an offset in the calorific value of around 50 - 80 J. This value has been validated by testing several samples in IC and by trial and error within the calorific value calculations. For a nitrogen correction without oxygen flushing an average of 20 – 40 J can be expected while if the bomb vessel is flushed, the nitrogen correction would be in the range of 2 - 8 J.

5. Conclusions

This study has provided the root causes behind poor reproducibility of calorific value determinations of solid biofuels. Moreover, a quantified analysis to each cause has been introduced. In optimum case, around 100 - 250 J reproducibility can be expected for wood chips. Reproducibility exceeding this value indicates some errors occurred during the sample preparation, measurements or corrections. By assuring EMC, sensitive handling and accurate calculations of the thermochemical corrections, the repeatability of the measurements significantly improves by up to 50%, while the reproducibility variation is minimized. Moreover, these improvements will be reflected upon the final expanded uncertainty to give a total uncertainty of around ± 1% (k=2, 95% coverage). The small margin of deviation between both the biomass provider and end-user will eventually lower the risks of having false estimation of cost. Therefore, it helps to fulfill the final objective of assuring a fair-trade policy.

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