Propagation of uncertainties and systematic errors in the measurements of long-lasting heat flows using differential scanning calorimetry

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Abstract Results from the measurement of the heat of reaction of hydrothermal carbonization by power compensated differential scanning calorimetry exhibited a comparably high experimental standard deviation of around 10–20%. The reasons for this standard deviation have been investigated and are being presented in this article. The zeroline deviation and its repeatability showed a decisive influence on the measurements due to the length of the thermal effects (several hours) and the experimental setup (high thermal capacity due to pressure capsules and hydrothermal conditions, type of calorimeter). It was quantified by reference runs and compensated mathematically. In addition, conceptual issues due to the propagation of uncertainty by sum operations are derived. There is an optimum peak length after which the uncertainty rises due to this uncertainty propagation. This optimum is at a signal level within the noise level. However, the contribution of this uncertainty showed little significance compared to the zeroline deviation and thus could be neglected. Results from hydrothermal carbonization of glucose show a mean value of 1060 J/g_{daf} with a standard deviation of 14% for the presented experimental setup. These values include compensations of systematic errors, including the zeroline deviation, baseline correction, leakage, and transient effects, which are discussed in detail.

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Abbreviations

DSC	Differential scanning calorimetry
HTC	Hydrothermal carbonization
Daf	Dry ash free
Rel	Relative (uncertainty)
Sys	Systematic (error)
σ	Standard deviation

Introduction

Being a reliable analysis method for the determination of caloric effects, power compensated differential scanning calorimetry (DSC) was applied to determine the heat of reaction of hydrothermal carbonization (HTC). Recently, this reaction has attended increased interest for the conversion of biomass to a coal-like substance [1–4]. It was published early that HTC is an exothermal reaction and its heat of reaction has been estimated based on a simplified stoichiometry [5]. The need of more detailed measurements has been identified and experimental investigations performed by calorimetric analyses [6] and by mass and energy balances [7]. However, residence times have been comparably short (several minutes) due to different intentions, which resulted in a heat of reaction close to zero. In contrast, hydrothermal carbonization reactions take place over a range of several hours. First measurements with a DSC of such long residence times were characterized by a comparably high standard deviation of up to 14%. The cause of this relatively high uncertainty has been investigated in detail and will be discussed and presented here.

Hydrothermal carbonization of biomass is a reaction that takes place in subcritical liquid water, usually at temperatures around 180–250 °C and a residence time of several

hours [3–5]. Dehydration and decarboxylation take place, yielding a solid product that closely resembles natural lignite except a higher content of oxygen-containing functional groups [8]. To achieve the necessary reaction conditions, closed crucibles have to be used that can withstand the vapor pressure of water at the investigated temperatures, i.e., pressures up to 40 bar. Due to this additional thermal mass of the pressure capsules and the amount of water present, any heat effects will be smeared. More important, the reaction is very slow leading to low heat flows (typically less than 5 mW), which are spread over a length of several hours (typically 4–6 h). In addition, sample weight is limited to about 4–6 mg due to the volume of the capsules.

In consequence, the influences of baseline determination and zeroline repeatability increase, which is being discussed first. The resulting issue of defining a peak end gives rise to more fundamental issues related to the propagation of uncertainties. These issues are addressed and quantified for the given application in the calorimeter used. Results from the chosen experimental setup of HTC of glucose are presented and two different evaluation methods are compared, focusing on systematic errors and their compensation.

Zeroline deviation and baseline determination

According to ISO 11357-1:1997, the baseline is defined as the "part of the recorded curve outside, but adjacent to, the reaction or transition zone. In this part of the recorded curve, the heat flux difference is approximately constant." It is used to derive a "virtual baseline" (most commonly by interpolating or extrapolating the baseline) which acts as reference for the calculation of the peak area of the investigated heat effect. Thus, the determination of the baseline and the choice of a virtual baseline are decisive for the result of a measurement.

The measured curve with empty crucibles is called zeroline and is a characteristic of each calorimeter. In theory, it should be equal to zero, however, it is not possible to produce such a perfectly symmetrical DSC and the zeroline will always deviate from zero [9]. This zeroline deviation can be adjusted to a certain extent in between two measurements. However, due to the length of a run of >20 h in the presented case, significant long term drift will always remain. In addition, the slope and magnitude of the zeroline are not repeatable between the runs (as will be shown below).

The influences of the zeroline deviation and the baseline determination depend on the temperature program used. Temperature scans have been applied for the presented case of HTC but the results could not be interpreted. The

reasons are most likely phase transition and dissolution of some of the (by)products in water at temperatures above 100 °C (both effects have been observed during other experiments). Therefore, isothermal runs have been used (i.e., the heat flow was measured as a function of time at constant temperature). In that case, the short term noise of the calorimeter should be higher than the long term drift [9]. Zerolines recorded by the used calorimeter showed a mean short term (1 min) peak-to-peak noise of 0.047 mW with a standard deviation of 0.030 mW (pressure capsules with the same amount of water without any sample have been subjected to 240° over 10 h). This noise level is more than one magnitude higher than the technical specification (which is still being met and has been confirmed by test runs without any crucibles). Already over the length of 1 h, the peak-to-peak drift was significantly higher at 0.110 mW with a standard deviation of 0.008 mW, mainly due to transient effects of the rapid heating in the beginning of the run. To assure a completely reacted sample, one run was set to 10 h. Over such a period the peak-to-peak drift rose to 0.265 mW with a standard deviation of 0.012 mW. Given these results, which were determined from six zerolines of each 10 h length, isothermal runs are not expected to give accurate results. Despite this inaccuracy, isothermal runs were performed due to the inconsistent data from temperature scans and the need to assess the heat of reaction for this specific case. This requires dealing with the zeroline deviation to reduce the inaccuracy of the result, as presented in the following sections.

Usually, the virtual baseline is created by an extrapolation of the heat flow after the reaction is completed for the case of isothermal runs [9]. Given a high repeatability of the zeroline, the heat flow should be constant after the reaction when the zeroline has been subtracted. This is not the case for the chosen experimental setup. There remains a certain slope once the reaction can be assumed to be completed. This slope cannot be used for an extrapolation because it stems from a low repeatability of the zeroline and therefore cannot be assumed to describe its behavior well enough to increase the accuracy of the result. In consequence, the baseline cannot be given a specific shape and it has to be assumed horizontal. This is a major drawback, because the error due to the (virtual) baseline uncertainty is directly proportional to the length of the measurement, i.e., comparably high for the discussed case: an uncertainty of ±0.01 mW can result in a deviation of the result of above ±40 J/g over the length of the reaction.

Reducing the interval of integration for the determination of the peak area can reduce this negative impact by a reduction of the zeroline deviation which tends to rise over time and thus indirectly by a reduction of the contribution of the error connected with the creation of the virtual baseline. In order to reduce the uncertainty connected with

the determination of the virtual baseline, it has to be concluded that it is important to define the start and the end of the peak of a heat effect (i.e., the interval of integration) rather than integrating over the whole range of data.

Uncertainty propagation by sum operations

Inevitably, the measurement signal of heat effects will disappear in the noise level of any calorimeter used at one point. Apart from the difficulties to determine this point, it cannot be avoided that there is a part of the measurement data which will not be considered for the calculation of the result despite the fact that it contains information from the heat effect investigated. These issues are increased by long-lasting heat effects and smeared data, which is the case discussed here. Theoretical considerations for the propagation of such uncertainties need to be derived in general and applied to DSC to allow for a quantification of these effects and to assess their significance.

Theory

It is known that sum operations are unfavorable for the propagation of uncertainties when compared to multiplication. They are inevitable for the calculation of areas below measured curves of an unknown function (numerical integration) as is the case for DSC measurements. However, the extent to which the propagation of uncertainty by sum operations contributes is not completely independent of the length of the interval of integration and hence of the evaluation method used. A derivation for the uncertainty propagation by Gauss for the integration of an interval of a measurement signal X shows that the overall uncertainty $U_{Y,\text{Gauss}}$ of the measurement result Y rises with the number of sum operations (n) performed, i.e., with the length of the interval of integration (under the assumption of a constant uncertainty of the measurements U_X):

$$Y = \int_0^t X(t)dt \approx \sum_{i=0}^n X(i)\Delta t \tag{1}$$

$$U_{Y,\text{Gauss}} = \sqrt{n \cdot (\Delta t \cdot U_X)^2} = \sqrt{n} \cdot \Delta t \cdot U_X \tag{2}$$

It should be emphasized that this is valid only for an increase of the integration interval and not for increasing the amount of calculation steps within a given interval (i.e., increasing the resolution of a measurement). The conclusion that can be drawn appears trivial at first sight: the integration interval should be limited to the range of data points which exhibit a measured signal. This result generally is independent of the function that describes the curve. However, it changes when considering the relative

uncertainty which is more meaningful than the absolute uncertainty. The relative uncertainty decreases with every increase of the interval of integration (i.e., with every additional measurement) for an arbitrary oscillation around a non-zero constant value. This can be shown by an analytical solution.

$$X(t) = a \cdot \sin(b \cdot t) + c \tag{3}$$

$$U_{Y,\text{gauss,rel}} = \frac{\Delta t \cdot U_X}{c\sqrt{n} \cdot \Delta t + \frac{a}{b\sqrt{n}}[1 - \cos(b \cdot n \cdot \Delta t)]} \tag{4}$$

However, if the parameter c is zero or decreases exponentially, the relative uncertainty increases for large values of n.

Application to differential scanning calorimetry

In many applications, it is necessary to determine a limited area below a measurement curve, as is the case for calorimetry. These areas are most often described by an exponentially shaped peak and therefore the issue of defining an interval of integration to reduce the relative uncertainty applies (see Eq. 4). At some point of the integration along the measurement curve, one will encounter an optimization problem because the relative contribution of the random uncertainty will become higher than the reduction of the systematic error due to the part of the area which is not covered by the integration (see also Fig. 3).

This issue is illustrated by an exemplary peak described by two exponential functions:

$$X(t) = a[\exp(b \cdot t) - \exp(c \cdot t)] \tag{5}$$
$$b, c \leq 0$$

The relative uncertainty is determined by the addition of the (known) systematic error due to the missing part of the peak area and the random uncertainty of the measurement signal propagated according to Eq. 2

$$U_{Y,\text{rel}} = \frac{U_{Y,\text{sys}} + U_{Y,\text{gauss}}}{Y}$$

$$= \frac{\left|a/c \exp(c \cdot n \cdot \Delta t) - a/b \exp(b \cdot n \cdot \Delta t)\right| + \left|\sqrt{n} \cdot \Delta t \cdot U_X\right|}{\left|a\frac{b-c}{b \cdot c}\right|} \tag{6}$$

It should be noted that Eq. 6 does not account for the subtraction of a zeroline. In case a repeated process is subtracted from the measurement signal (according to the procedure of ISO 11357-5:1999), the contribution of the random uncertainty rises by a factor of $\sqrt{2}$ due to the addition of another sum operation according to Eqs. 1 and 2.

In Fig. 1, a relatively broad peak of several hours that represents a curve fit to experimental data obtained from an
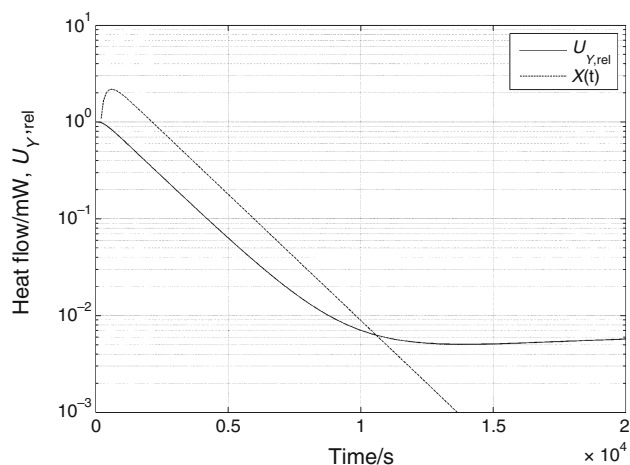
Fig. 1 Development of the relative uncertainty of the calculation of a peak area $U_{Y,\text{rel}}$ over the length of the interval of integration. The shape of the peak $X(t)$ is illustrated to allow for an orientation

HTC reaction ($a = 3.3907$; $b = -0.0047$; $c = -0.0006$) is shown as broken line. The uncertainty of this measurement signal U_X has been determined by measuring the noise level of the calorimeter (see below). A confidence interval of 3σ has been chosen for the quantification of the uncertainty of the measurement signal, which gave $U_X = \pm 0.2$ mW. Using this uncertainty, Eq. 6 was evaluated and plotted as solid line.

The measurement signal falls below the noise level at around 120 min. However, the minimum of the relative uncertainty is reached later. It has been determined by iteration to be around 240 min. At that time the value of the measurement signal is 0.6 µW, i.e., two orders of magnitude below the standard deviation of the measurement signal. Thus, the intuitive condition that a signal below the noise level is meaningless and should be rejected is not supported by this result.

Finally, the relative uncertainty is below 1% after 150 min. It rises over 1%, but only after a sampling time of 600 min. The conceptual contribution of the length of the interval of integration holds no significance for the case investigated (although it rises constantly for n approaching infinity (see Eq. 6)).

Although this uncertainty analysis has been performed on a generalized basis, it should be emphasized that its relevance is low for most applications of DSC because the impact of the described issue decreases with a lower noise level of the experimental setup used as well as with shorter and higher peaks (which represent the most common applications). However, in case of the investigation of long-lasting, smeared heat effects it is recommended to analyze the development of the relative uncertainty over the length of the integration interval prior to evaluating the data.

Experimental section

The measurements were conducted in order to determine the heat of reaction of hydrothermal carbonization, a reaction that lasts several hours (typically 4–6 h).

Apparatus and experimental procedure

A power compensated differential scanning calorimeter from PerkinElmer (DSC-7) with stainless steel high pressure capsules has been used for the calorimetric measurements. The preparation, conduction, and evaluation of all experiments followed ISO 11357-1:1997 and ISO 11357-5:1999 using the isothermal method (test runs with temperature scans could not achieve reproducible results). Each test run was conducted with the nominal temperature being held for 10 h to assure a completed reaction (the reaction time was expected to be between 4 and 6 h). The reference capsule was filled with the same mass of distilled water as the sample mass. The tightness of both the reference and sample capsule was checked after each run by a determination of the weight difference. The cooler temperature was held at 20 °C by a thermostat/kryostat (Lauda RC6CS). The nitrogen purge gas flow was set at 1.3 bar.

Materials for calibration (Indium and Tin) and glucose were purchased as standard grade chemicals from Carl Roth GmbH+ Co. KG.

The determination of the water content of cellulose and glucose was conducted according to the oven dry method of DIN CEN/TS 14774-1:2004 (the sample was dried at 105 °C until stability of the mass was reached). This water content was assumed to be constant, because the laboratory was air-conditioned to meet reference conditions (20 °C, relative humidity $\phi = 40\%$; this assumption has been checked by repeated determination of the water content at a later stage of the experiments).

Evaluation method

It was decided to implement a self-written data evaluation in order to keep control of some of the uncertainties connected with the procedure. The recorded data from the calorimeter already includes corrections of the temperature and heat flow scales, the subtraction of the zeroline has been performed after that correction. The start of the interval of integration (i.e., the relevant length of the peak) was determined by the initial transition effects. These have been amplified by the use of the pressure capsules filled with water, both of which exhibit an undesirably high heat capacity. The transitional effects have been reproducible with an acceptable precision (± 0.5 mW) just after 90 s. The start of the interval of integration thus was set to 100 s.

Statistical methods were chosen to determine the end of the interval of integration. A one-sample location test (z-test) with a confidence interval of 95% was applied. Statistically significant data (i.e., measured heat flow) existed as long as following test condition T was met [10]:

$$T = \left| \frac{\bar{x} - \mu_0}{\sigma_0} \sqrt{n} \right| > z_{1-\alpha/2} \tag{7}$$

The z value is fixed at $z_{1-\alpha/2} = 1.96$ for a confidence interval of 95% [10]. All other parameters have been determined as follows: samples of 100 consecutive data points have been evaluated (i.e., n = 100) and their mean value, $\bar{x}$, calculated. The expected value μ_0 was determined by the mean value of the data points of the last hour of each run. The standard deviation σ_0 has been determined by the reference experiments for the investigation of the zeroline deviation mentioned below: the difference of two consecutive runs (representing the procedure of ISO 11357-5:1999) has been calculated and the standard deviation of the result determined. This procedure has been performed six times in total and the highest standard deviation ($\sigma_0 = 0.067$ mW) was used in Eq. 7.

The baseline was determined by the mean value of 1 h of data points consecutive to the previously determined end of the peak and assumed to be horizontal.

Results and discussion

The results of the heat of reaction of HTC of glucose and its experimental uncertainty are illustrated in Fig. 2. Table 1 summarizes the heat of reaction resulting from the implemented evaluation method compared to an integration over the complete set of data. All data are only valid for the chosen experimental setup.
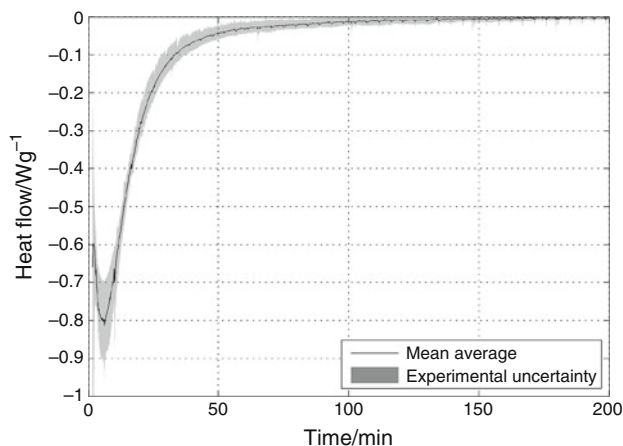

Fig. 2 Development of the standard deviation and mean average of the zeroline deviation of six reference runs at 240 °C over the length of the run

Table 1 Results from the measurement of the heat of reaction of hydrothermal carbonization of glucose at 240 °C comparing two different methods of data evaluation

	ΔH/J g_{daf}^{-1} (z-test)	ΔH/J g_{daf}^{-1} (complete integration)
#1	−910	−890
#2	−1180	−1030
#3	−1180	−1190
#4	−850	−730
#5	−1180	−1200
#6	−1060	−970
Mean value	−1060	−1000
σ/%	14	18

It becomes evident that the standard deviation is increased significantly by an integration over a longer period. Simultaneously, the mean average decreases to some extent. From statistics, one has to conclude that this lower result is closer to the expected value due to the consideration of additional measurement data. However, this picture changes when physical considerations are included. No endothermal reactions are expected after initial hydrolysis, i.e., by considering heat flows that are not accounted for due to the limited interval of integration, the exothermal heat must rise. As this is not the case, it has to be concluded that this difference in the mean average stems from the deviation of the zeroline. Therefore, it could be reasoned that the result from a shorter interval of integration is both more precise and closer to the expected value than an integration of the complete set of data—even though a part of the measurement information is not contributing to the result.

Systematic errors

Different systematic errors have been determined and quantified. In contrast to the previously discussed uncertainty of the integration, they are only valid for the particular calorimeter and evaluation method used. Although these systematic uncertainties are in a significant order of magnitude, they compensate each other in this specific case. Including systematic errors, the result of the heat of reaction of glucose carbonized at 240 °C remains at −1060 J/g with a standard deviation of 14%. Nevertheless, systematic errors will be discussed briefly for completeness.

Integration offset

To quantify the systematic uncertainty connected with the delayed start of the integration interval (see section "Evaluation method"), the heat flow signal was assumed to

Fig. 3 Illustration of the determination of the peak area including the virtual baseline and zeroline subtraction. Also, the two systematic errors $U_{Y,\text{sys,offset}}$ and $U_{Y,\text{sys,base}}$ are shown. Note that the scales have been adjusted individually to increase the informative value of the figure and do not represent actual order of magnitudes when compared to each other
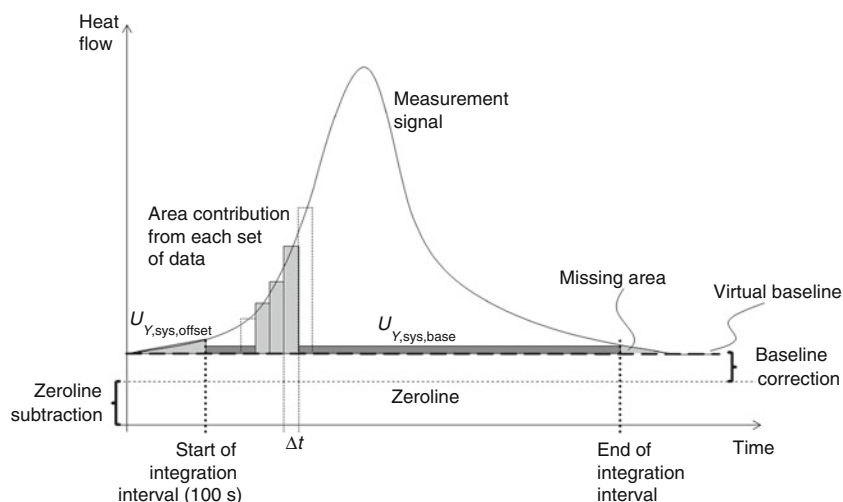
show exponential behavior. Any approximation to quantify this amount of heat has to be inaccurate; it was chosen to estimate its maximum value by the area described by a linear interpolation between the value at the start of the integration interval and zero (see also Fig. 3).

$$U_{Y,\text{sys,offset}} = \frac{\left[\dot{Q}(100s)\right] \cdot 100s}{2} \quad (8)$$

It differs for each test run and naturally increases at higher temperatures due to an acceleration of the reaction. Calculated values are within 10–30 J/g for glucose carbonized at 240 °C.

Baseline correction

The baseline approaches the expected value of the noise level very close due to the amount of data used for its determination. Errors due to a horizontal baseline instead of a more characteristic shape cannot be accounted for and affect the final results significantly. However, a systematic error can be quantified that stems from the condition used for the determination of the end of the peak. This condition systematically leaves a part of the heat flow unconsidered, more precisely any set of data, whose sample mean is below the criterion of the one-sample location test.

$$\bar{x} = \frac{z_{1-\alpha/2} \cdot \sigma_0}{\sqrt{n}} = 0.013 \text{ mW} \quad (9)$$

Thus, the systematic error of the baseline determination due to the condition for the peak end is characterized by a rectangular area (see also Fig. 3).

$$U_{Y,\text{sys,base}} = 0.013 \text{ mW} \cdot t_{\text{int}} \quad (10)$$

Depending on the length of the interval of integration t_{int}, the systematic error due to the baseline determination was within 10–50 J/g.

Zeroline deviation

In addition to the previously mentioned short term noise and long term drift of the zeroline, the repeatability of the zeroline is of interest to determine its influence on the measurement result. It is characterized by a peak-to-peak scatter of ±0.627 mW. Moreover, the area of the zeroline due to this deviation has been calculated as a function of time. This calculation has been performed after the subtraction of two consecutive runs in order to achieve a result that is meaningful for the experiments performed. The baseline for this calculation has been determined by the mean average of 1 h of data points starting from the point to which the deviation has been determined (this procedure has also been used for the evaluation of measurement data).

Six reference runs (zerolines) at 240 °C have been performed in total. The mean value of the deviation of these six zerolines as well as their standard deviation is shown in Fig. 4. A steady rise of the standard deviation can be observed which has been explained by Eq. 2. The mean value of the zeroline tends to be below zero, with a maximum of its absolute value around 360 min. It should be noted that this is not the case for the individual zerolines, whose deviation tends to rise over time. Both observations are consistent with the theoretical considerations presented above.

The systematic zeroline deviation of a set of runs as illustrated in Fig. 4 has been compensated for by a linear approach within the range of 100–19,000 s (which represents the range of the interval of integration determined by the used evaluation method in the case of glucose carbonized at 240 °C).

$$U_{Y,\text{sys,zeroline}} = -0.03 \text{ mW} \cdot t \quad (11)$$

The quantification of the zeroline deviation cannot be assigned to a single experimental run because it has been calculated as the mean value for a set of data, i.e., only its
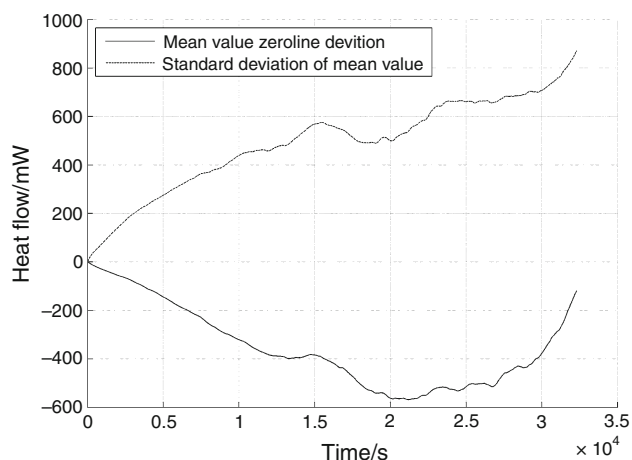
Fig. 4 Graphical illustration of the results from the calorimetric measurements of the heat of reaction of hydrothermal carbonization of glucose at 240 °C

mean average of −60 J/g includes valid information and is subtracted from the mean average of the separately corrected results of Table 1.

Leakage

In case a leak was detected after a run, the results were still used when its influence on the result was acceptable. The error due to a leak has been approximated by multiplying the mass difference of the filled and sealed pressure capsule before and after a run with the heat of evaporation of water at 240 °C (1766 J/g [11]). Systematic errors due to leakage have been accepted up to 50 J/g. In case of higher losses, the experiment has been rejected.

Comparison/proof of consistency

The systematic errors discussed above can also be used to correct the result of a complete integration (see Table 1). In that case, the baseline correction $U_{Y,sys,base}$ (see Eq. 10) does not apply because the z-test has not been applied. It should be noted that the systematic error due to the zeroline deviation is much smaller (see Fig. 2) and its mean average has been determined to −22 J/g. The result for glucose carbonized at 240 °C using the method of complete integration including systematic errors is −1070 J/g$_{daf}$ with a standard deviation of 13%. It is concluded that the considered systematic errors represent the major errors that occurred and that the methods are consistent to each other. Additionally, this result supports the observation which has been concluded from Table 1—the higher result must be the one closer to the expected value.

Based on these results, the comparably high noise level which has been observed for the used calorimeter (see

above) is regarded to have a negligible influence on the measurement uncertainty compared to the influence of the zeroline deviation.

Conclusions

In order to determine long-lasting (4–6 h) smeared heat effects, power compensated differential scanning calorimetry has been applied. The standard deviation of the results (around 10–20%) is high compared to the typical accuracy of such measurements. The reason for this uncertainty is mainly due to the zeroline deviation and its repeatability as a specific characteristic of the experimental setup (high thermal capacity due to pressure capsules and hydrothermal conditions, type of DSC).

The issue of defining a peak end for the smeared curve has been addressed and it was shown by fundamental theoretic considerations how the definition of the peak end affects the propagation of uncertainties. There is an optimum peak length after which the uncertainty rises due to the propagation of uncertainties in sum operations. This optimum is at a signal level within the noise level. To evaluate the statistical significance of such low level signals, a one-sample location test (z-test) was successfully applied as criterion. However, the contribution of this uncertainty propagation is not significant compared to the zeroline deviation for the presented case.

In addition, a set of systematic errors has been identified and quantified for the presented experimental setup, including the zeroline deviation, baseline correction, leakage, and transient effects. The consistency of these errors has been checked and it was shown that they represent the most significant contribution.

Hydrothermal carbonization of glucose at 240 °C has been characterized by this particular experimental setup with a heat of reaction of −1060 J/g$_{daf}$. This value has been determined with a standard deviation of 14%.

References

1. Titirici MM, Thomas A, Antonietti M. Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO$_2$ problem? New J Chem. 2007;31:787–9.

2. Hu B, Yu S, Wang K, Liu L, Xu X. Functional carbonaceous materials from hydrothermal carbonization of biomass: an effective chemical process. Dalton Trans. 2008;40:5414–23.

3. Titirici M, Antonietti M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. Chem Soc Rev. 2010;39:103–16.

4. Funke A, Ziegler F. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. Biofuels Bioprod Biorefin. 2010;4:160–77.

5. Bergius F. Die Anwendung hoher Drücke bei chemischen Vorgängen und eine Nachbildung des Entstehungsprozesses der Steinkohle. Halle a. d. Saale: Wilhelm Knapp; 1913.p. 41–58.

6. Sunner S. Measurements on heat effects accompanying the wet carbonization of peat in the temperature range 20 to 220 degrees C. Acta Polytechnica Scandinavica—Chemistry Including Metallurgy Series no. 14; 1961.

7. Yan W, Hastings JT, Acharjee TC, Coronella CJ, Vasquez VR. Mass and energy balance of wet torrefaction of lignocellulosic biomass. Energy Fuels. 2010;24:4738–42.

8. Sugimoto Y, Miki Y. Chemical structure of artificial coals obtained from cellulose, wood and peat. In: Ziegler A, van Heek KH, Klein J, Wanzl W, editors. Proceedings of the 9th International Conference on Coal Science ICCS'97, 1997; vol. 1. p. 187–190.

9. Höhne GWH, Flemminger WF, Flammersheim H. Differential scanning calorimetry. New York: Springer Verlag; 2003.

10. Toutenburg H, Schomaker M, Wißmann M, Heumann C. Arbeitsbuch zur deskriptiven und induktiven Statistik. Berlin, Heidelberg: Springer Verlag; 2009.

11. VDI Wärmeatlas. New York: Springer Verlag; 2006.