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Influence of the emissivity of the sample on differential scanning calorimetry measurements

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Abstract

A possible cause of the wide differences present in the literature values for the calorimetric measurements of the pyrolysis heat of biomass was analyzed. The apparent specific heat of char from pyrolysis of beech wood was investigated by means of a differential scanning calorimeter (DSC). The objective was to find out the influence of the use of a lid on the crucible on the experimental results. In a first experimental series, the crucible containing the sample and the empty reference crucible were closed by a pierced lid. In a second experimental series, the crucible containing the sample and the reference crucible were used without a lid. Results of experiments within the same series showed excellent agreement, but the results of the first series were completely different with respect to those of the second series. A possible explanation for these differences are the different emissivities of the crucible material (aluminium) and char. During experiments without a lid a different radiative heat exchange occurs between the two crucibles and the opposite wall of the DSC measurement cell. In order to confirm the effect of heat radiation inside the DSC measuring cell, additional experiments with aluminium oxide and graphite were carried out.

Keywords: Differential scanning calorimetry; Biomass pyrolysis; Radiation; Specific heat measurements; Radiating heat transfer

1. Introduction

As a renewable source wood becomes increasingly important for the production of energy. An improvement of the efficiency of energy production processes requires a detailed knowledge of the thermal conversion process. As reported in [1,2], heat of pyrolysis has an important influence on the course of thermal conversion. Differential scanning calorimetry (DSC) is a well-established method which is used in various fields [3]. However, the reported values of calorimetric measurements for the determination of the heat of pyrolysis of wood are very different [4–6]. Endothermic but also large exothermic values are reported. In the present work, one of the possible causes is pointed out for the wide differences of the reported values for heat of pyrolysis.

In experiments carried out by DSC techniques, the samples are usually fitted into crucibles which are closed by a lid. In order to avoid crucible pressurization due to gas phase thermal expansion at high temperatures and to the possible formation of

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Nomenclature

A	radiating surface (m^2)
c_p	specific heat of the sample ($J\ g^{-1}\ K^{-1}$)
dT/dt	heating rate ($K\ s^{-1}$)
m	sample mass (g)
M_c	crucible mass (g)
T	temperature (K)

Greek letters

ε	emissivity radiation constant ($W\ m^{-2}\ K^{-4}$)
φ	specific heat flow rate obtained from baseline corrected DSC measurements ($W\ g^{-1}$)
φ_d	specific heat flow rate obtained in the experiments using samples in both the sample crucible and the reference crucible ($W\ g^{-1}$)
φ_t	calculated specific heat flow rate ($W\ g^{-1}$)
φ^*	radiation corrected specific heat flow rate obtained from Eq. (8) ($W\ g^{-1}$)
Φ	heat flow rate obtained from baseline corrected DSC measurements (W)
Φ_{bu}	heat flow rate of radiation from a body 'b' to the surroundings 'u' (W)
Φ_R	radiating heat flow rate from the reference crucible to the cover of DSC measuring cell (W)
Φ_S	radiating heat flow rate from the sample to the cover of DSC measuring cell (W)
$\Delta\Phi_{exp}$	difference of the measured heat flow rates between experiments with and without a lid (W)
$\Delta\Phi_{mod}$	difference of the calculated heat flow rates between experiments with and without a lid (W)
ΔT_{rad}	temperature difference between T_S and T_l (K)

Subscripts

b	body
c	crucible
l	cover of the DSC measurement cell
n	experiment without lid
y	experiment with lid
R	reference crucible
S	sample
u	surroundings

volatiles, the lid is usually pierced or provided with small openings. However, in the pyrolysis of wood, secondary reactions between volatile pyrolysis products and primary char were observed (e.g. [7,8]). Therefore, experiments using crucibles without lid were performed by some authors (e.g. [9,10]). In these experiments, the removal of the volatile primary products is easier and the extent of secondary reactions, that may influence the heat of reaction, is reduced. Important differences were detected carrying out DSC experiments on wood using crucibles with and without a lid. Since the results were completely different, the aim of the present work was to shed some light on one of the possible reasons for these differences.

Experiments were carried out on char obtained from the pyrolysis of beech wood at low heating rates ($10\ K\ min^{-1}$). Additional experiments using aluminium oxide and graphite were carried out to validate the results obtained.

2. Experimental

2.1. Techniques

DSC experimental data were obtained using a Mettler DSC 25 calorimeter. Constant heating rate (348–773 K, $10\ K\ min^{-1}$) experimental runs were performed using nitrogen as the purge gas ($300\ ml\ min^{-1}$). Typical total sample masses of about 2–10 mg were used. The DSC runs were performed using aluminum crucibles with or without a pierced lid, as specified in the followings. The same sample was used for experiments with and without lid.

2.2. Materials

Experimental runs were performed on beech wood char obtained directly in the DSC instrument following the procedure described below. Aluminium oxide powder (size fraction: 90–120 μm) and graphite powder (size fraction: 250–750 μm) were provided by Aldrich (Milan). A beech wood powder (particle size: 250–500 μm) was obtained by means of a hammermill. About 8 mg of dry beech wood particles were pressed into a compact disc of the same diameter as the DSC crucible. The beech wood char was produced heating the wood sample in the DSC up to 773 K in nitrogen at a heating rate of 10 K/min. The sample was kept at 773 K for 10 min in order to ensure the completeness of pyrolysis. A sample of about 2 mg of char was obtained by this procedure.

3. Results and discussion

Char specific heat measurements were carried out by constant heating rate (10 K min^{-1}) DSC runs in pure nitrogen. Two series of experiments were carried out on char samples. In series 1, all crucibles were closed by a lid. In series 2, only crucibles without a lid were used. All other conditions (heating rate, temperature range, sample mass, nitrogen flow) were the same for the two experimental series. All the heat flow curves of series 1 were corrected by baselines obtained from runs with empty crucibles which were closed by a lid and those of series 2 were corrected by baselines obtained from runs with empty crucibles without a lid.

Fig. 1 shows the specific heat flow rate curves which were obtained from DSC experiments. Runs 1 and 2 are typical results obtained in series 1 (crucible closed by a lid), and runs 3 and 4 are typical results of series 2 (crucible without a lid). Considering the characteristics of the DSC experiments, the reproducibility is satisfying. The figure also shows the calculated specific heat flow rate, φ_t, estimated on the basis of literature data for the specific heat of char [11] using the following expression:

$$\varphi_t = c_p(T)\frac{dT}{dt} \qquad (1)$$

where c_p is the sample specific heat capacity and dT/dt the heating rate of the experimental run.

It can be seen in Fig. 1 that the results of runs 1 and 2 are in good agreement with the calculated heat flow rate. However, the results of runs 3 and 4 show an increasing endothermic difference from the calculated curve with increasing temperature. The reason for these differences between experiments with and without a lid can be attributed to the different emissivities of char and the material of the reference crucible. Due to the higher emissivity of char compared with the emissivity of aluminium, the heat flow rate of radiation from the char sample to the opposite wall of the instrument (the cover of the DSC measurement cell) is higher than the one of the reference crucible (see Fig. 2).

According to [12], the heat flow rate of radiation Φ_{bu} between a body 'b' and its surroundings 'u'

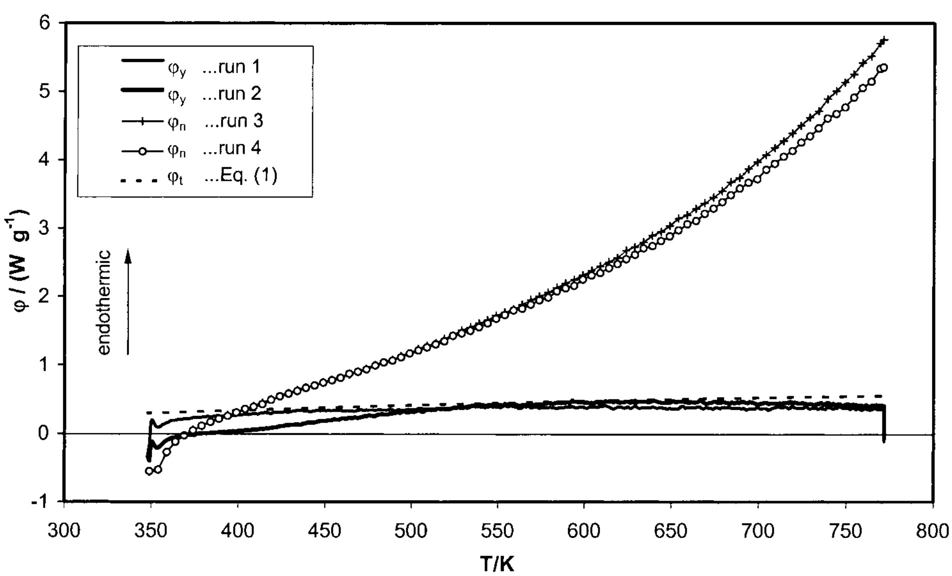

Fig. 1. Specific heat flow rates from DSC experiments with char from pyrolysis of beech wood, runs 1 and 2: crucible with a lid (φ_y); runs 3 and 4: crucible without a lid (φ_n).

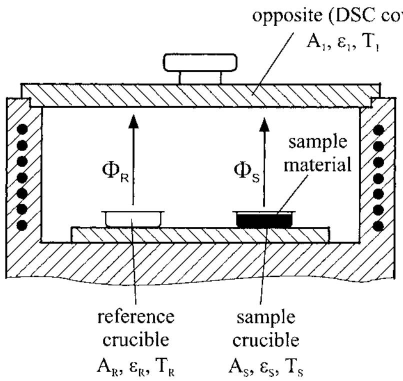

Fig. 2. Heat exchange by radiation between sample, reference crucible, and DSC cover inside the DSC measurement cell (schematic).

which completely covers the body can be described by Eq. (2)

$$\Phi_{\rm bu}=\frac{\sigma}{(1/\varepsilon_{\rm b})+(A_{\rm b}/A_{\rm u})((1/\varepsilon_{\rm u})-1)}A_{\rm b}(T_{\rm b}^4-T_{\rm u}^4) \qquad (2)$$

where σ is the radiation constant, ε the emissivity, A the radiant surfaces, and T the temperatures. With respect to Fig. 2, the body (b) is represented by the sample (S) or reference (R) crucible, and the surroundings (u) by furnace cover (l).

Thus, accounting for radiating heat contribution between the crucible lids and the instrument cover, the heat flow rate measured in a DSC experimental run may have the following expression:

$$\Phi=\left[(mc_{\rm p}+M_{\rm S,c}c_{\rm p,c})\frac{{\rm d}T}{{\rm d}t}+\Phi_{\rm S}\right]-\left[M_{\rm R,c}c_{\rm p,c}\frac{{\rm d}T}{{\rm d}t}+\Phi_{\rm R}\right] \qquad (3)$$

where $c_{\rm p}$ is the sample specific heat capacity, $c_{\rm p,c}$ the specific heat capacity of the crucible material, m the sample mass, $M_{\rm S,c}$ the mass of the sample crucible, $M_{\rm R,c}$ the mass of the reference crucible, dT/dt the heating rate, $\Phi_{\rm S}$ and $\Phi_{\rm R}$ the radiating heat flow rates from the crucibles to the DSC instrument cover, as expressed by Eq. (2). Since the sample and reference crucible mass should be the same, Eq. (3) may be simplified as follows:

$$\varphi\equiv\frac{\Phi}{m}=c_{\rm p}\frac{{\rm d}T}{{\rm d}t}+\frac{\Phi_{\rm S}-\Phi_{\rm R}}{m}=\varphi_{\rm t}+\frac{\Delta\Phi_{\rm mod}}{m} \qquad (4)$$

where $\Delta\Phi_{\rm mod}$ is the difference between the radiating heat flows. $\Delta\Phi_{\rm mod}$ is usually neglected, since when a lid is used, the emissivities of the sample and reference crucibles are the same. Nevertheless, the value of $\Delta\Phi_{\rm mod}$ may be calculated on the basis of Eq. (2). In conventional DSC instruments, as the Mettler DSC 25 used in these experiments, sample and reference temperature are never the same: the principle of heat flow measurement in these instruments is based on a small temperature difference between the sample and the reference crucible. However, the temperature difference between the crucibles may be estimated on the basis of the heat flow rate curve: for the results in Fig. 1, using the data provided by Mettler, a temperature difference of <0.2 K is present between the crucibles. If it is assumed that the difference between sample temperature $T_{\rm S}$ and reference temperature $T_{\rm R}$ is negligible and that the sample surface $A_{\rm S}$ is equal to the reference surface $A_{\rm R}$, then the difference in the heat flow rate of radiation of the sample surface and the reference surface can be described by the following equation:

$$\Delta\Phi_{\rm mod}=\Phi_{\rm S}-\Phi_{\rm R}=\left[\frac{1}{(1/\varepsilon_{\rm S})+(A_{\rm S}/A_{\rm l})((1/\varepsilon_{\rm l})-1)}-\frac{1}{(1/\varepsilon_{\rm R})+(A_{\rm S}/A_{\rm l})((1/\varepsilon_{\rm l})-1)}\right]\times\sigma A_{\rm S}(T_{\rm S}^4-T_{\rm l}^4) \qquad (5)$$

Table 1 lists the values of the emissivities of the substances investigated. Also, the values of the sample surfaces (the whole bottom cross section area of the crucible is taken), the bottom area of the empty reference crucible, and the surface of the opposite wall (the cover of the DSC measurement cell) are given. Obviously, if sample and reference emissivities are equal ($\varepsilon_{\rm S}=\varepsilon_{\rm R}$), $\Delta\Phi_{\rm mod}$ is 0. Thus, if a lid is used in DSC measurements, $\Delta\Phi_{\rm mod}$ is negligible since the emissivities of crucible lids may be considered equal if sample and reference crucibles are of the same material. On the other hand, if a lid is not used, the sample material and the empty reference crucible of the DSC may have different emissivities. Therefore $\Delta\Phi_{\rm mod}$ influences the results of DSC measurements, as shown in Eq. (4).

Fig. 1 shows that the experiments carried out without a lid on the crucibles show an apparently higher

Table 1
Emissivity, specific heats and surface areas of samples, reference crucible, and DSC cover

Substance	Surface A (mm^2)	Emissivity ε	Specific heat c_p ($J\ g^{-1}\ K^{-1}$)	
Aluminium, reference crucible	19.63	0.09 [14]	–	
Char sample, carbon	19.63	0.8 [13]	$c_p = \frac{8314}{5.75}\left[\exp\left(\frac{380}{T_S}\right)\left(\frac{\exp(380/T_S)-1}{380/T_S}\right)^{-2} + 2\exp\left(\frac{1800}{T_S}\right)\left(\frac{\exp(1800/T_S)-1}{1800/T_S}\right)^{-2}\right]$	[11]
Aluminium oxide, powder, 90–120 μm	19.63	0.46 [14]	$c_p = \frac{4.1868}{101.94}\left[22.08 + 0.00897T_S - \frac{522500}{T_S^2}\right]$	[13]
Graphite powder, 250–750 μm	19.63	0.98 [14]	$c_p = \frac{4.1868}{12.01}\left[2.673 + 0.002617T_S - \frac{116900}{T_S^2}\right]$	[13]
Opposite surface (DSC cover), silver, polished	415.5	0.052 [14]	–	

endothermic specific heat flow rate than the ones with a lid. Since the only difference in the experiments with and without a lid in Fig. 1 should be the different value of $\Delta\Phi_{mod}$, this suggests that in the experimental runs $\Delta\Phi_{mod}$ value is positive. As shown in Table 1, sample emissivity is higher than reference crucible emissivity. Thus, if $\Delta\Phi_{mod}$ is positive, the temperature of the cover of the DSC measurement cell should have been lower than the temperature of the sample and reference crucibles, so that positive values of Φ_S and Φ_R are obtained, as shown in Fig. 2. While furnace walls are directly warmed by means of heating elements, the cover is only heated by conduction, convection and radiation from the furnace walls. Thus, its temperature may well be lower than that of the sample and reference crucibles. Therefore, since the char sample has a higher emissivity, it emits more heat than the reference crucible and an apparent endothermic heat of reaction is deceived during the measurements.

In Fig. 3, $\Delta\Phi_{exp}$ obtained from experimental data in Fig. 1 is shown. $\Delta\Phi_{exp}$ was calculated as follows from the experimental runs performed on char samples:

$$\Delta\Phi_{exp} = \Phi_n - \Phi_y = m(\varphi_n - \varphi_y) \quad (6)$$

where subscript 'n' indicates the result of an experiment performed without lid, and subscript 'y' the result of an experiment performed with lids. Fig. 3 shows good agreement between the experimental heat flow rate $\Delta\Phi_{exp}$ and the calculated $\Delta\Phi_{mod}$. The figure also reports the temperature difference $\Delta\Phi_{rad}$ defined as

$$\Delta T_{rad} = T_S - T_l \quad (7)$$

where T_S is the sample temperature and T_l the temperature of the cover of the DSC measurement cell. The value of T_l was assumed in order to fit the calculated heat flow difference $\Delta\Phi_{mod}$ and the measured $\Delta\Phi_{exp}$. The almost linear increase of the temperature difference ΔT_{rad} and its estimated absolute value, as high as 8.8 K at 773 K, are worth noting.

Fig. 4 shows the specific heat flow rates obtained from experiments with aluminium oxide powder, using crucibles with and without a lid in the temperature range of 348–773 K at a heating rate of 10 K min^{-1}. Fig. 4 also shows the calculated specific heat flow rate φ_t estimated using the specific heat of aluminium oxide according to [13]. The figure also reports the specific heat flow rate φ^*, which is obtained subtracting the radiating heat flow rate $\Delta\Phi_{mod}$ from the results of the experiment performed on an aluminium oxide sample without a lid

$$\varphi^* = \varphi_n - \frac{\Delta\Phi_{mod}}{m} \quad (8)$$

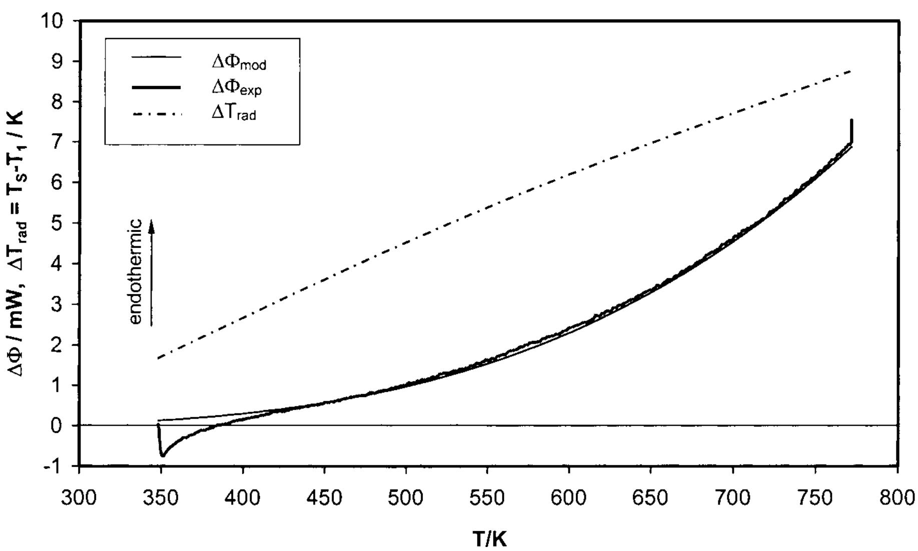

Fig. 3. Difference in heat flow rate between experiments with (φ_y) and without (φ_n) a lid using char from pyrolysis of beech wood ($\Delta\Phi_{exp}$: measured, and $\Delta\Phi_{mod}$: calculated).

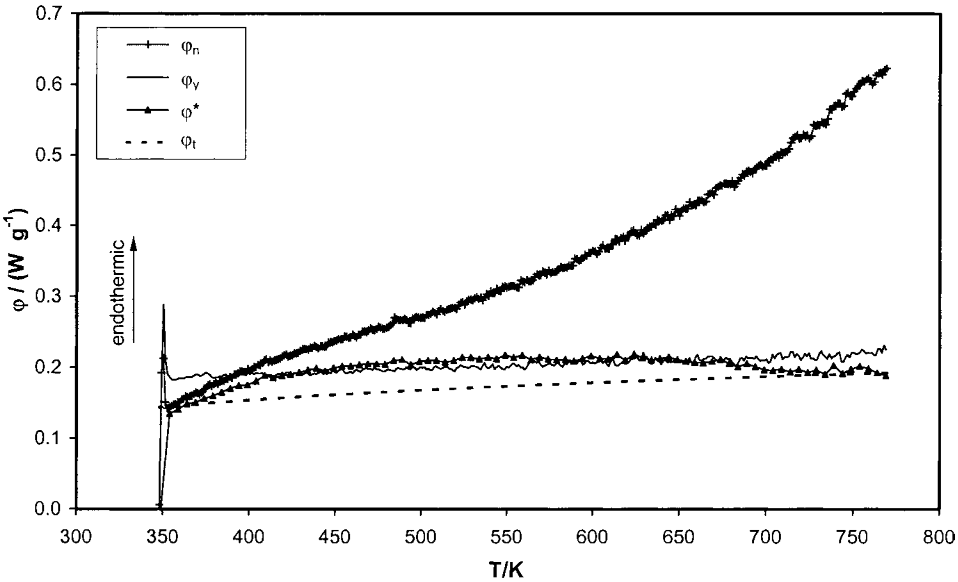

Fig. 4. Specific heat flow rates obtained from experiments with (φ_y) and without (φ_n) a lid using aluminium oxide powder; φ^*: specific heat flow rate from experiment without a lid corrected by the heat of radiation according to Eq. (3); φ_t: calculated specific heat flow rate for aluminium oxide.

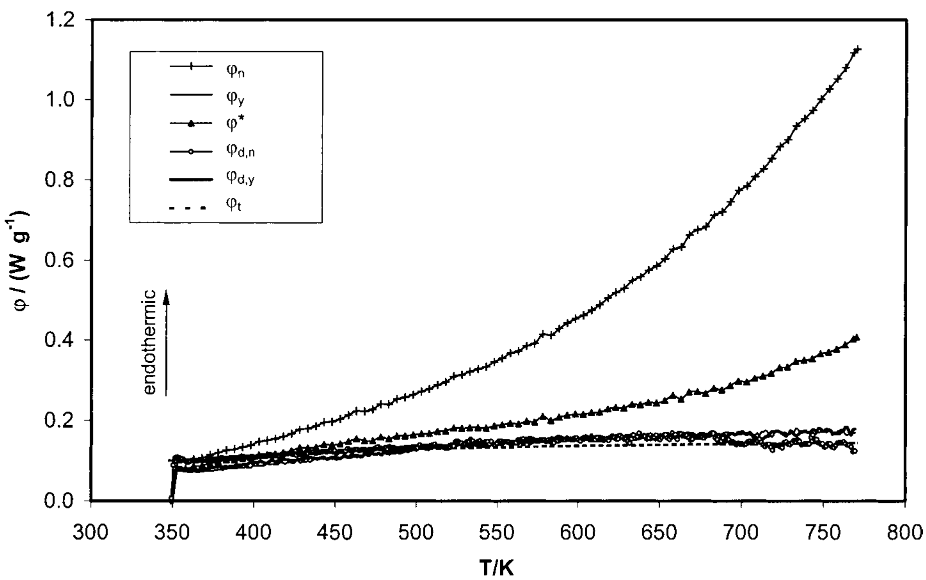

Fig. 5. Specific heat flow rates obtained from experiments with (φ_y) and without (φ_n) a lid using graphite powder; φ^*: specific heat flow rate from an experiment without a lid corrected by the heat flow rate of radiation; φ_t: calculated specific heat flow rate for graphite; φ_d: experiments using graphite powder in both the sample and the reference crucible.

The temperature difference ΔT_{rad} was assumed to be the same as in the experiments using char. The value of the corrected specific heat flow rate, φ^*, is in good accordance with the results of the experiment performed on aluminium oxide using a crucible with a lid, φ_y. The value of φ^* is also sufficiently near to the values reported in literature on the basis of Eq. (1) and of c_p values reported in Table 1.

Fig. 5 shows the specific heat flow rates obtained from experiments with graphite powder using crucibles with and without a lid in the temperature range of 348–773 K at a heating rate of 10 K min^{-1}. The figure also reports the calculated specific heat flow rate φ_t obtained using literature data for the specific heat of graphite [13]. The specific heat flow rate φ^* which is calculated by subtracting the heat flow rate of radiation $\Delta\Phi_{mod}$ from the results of the experiment performed without a lid is also shown in this figure. Again, the temperature difference ΔT_{rad} was assumed to be the same as in the experiments using char. The accordance of the corrected specific heat flow rate with the specific heat flow rate from the experiment using a crucible with a lid is not as good as for aluminium oxide. Uncertainties in the values of the emissivities may explain these differences. Therefore, calibration runs are important to quantify the impact of the heat of radiation on the DSC results. In Fig. 5 the specific heat flow rates φ_d are presented. These curves were obtained from experiments with graphite powder using different quantities of graphite powder in both, the sample crucible and the reference crucible. A higher quantity of sample was positioned in the sample crucible, but also the reference crucible was covered with a homogeneous layer of graphite powder. Thus, the apparent sample mass used to calculate the specific heat flow rates was the difference between the mass in the sample crucible and the mass in the reference crucible. However, both crucibles should have the same emissivity, either in the presence or in the absence of a lid. As shown in Fig. 5, the radiation effect is eliminated by this method.

4. Conclusions

The use of crucibles without a lid may be necessary in DSC runs if reaction conditions require a fast gas exchange between sample and its surroundings (e.g. in order to limit secondary reactions in the pyrolysis of wood). If sample and reference material have different emissivities, the influence of the heat flow rate of radiation has to be considered for a correct interpretation of DSC results. Neglecting this effect may lead to important errors if measurements are performed without a lid and the sample is directly exposed to a radiative heat exchange with the opposite wall of the instrument.

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