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A method to determine the course of heating value and heat production rate of volatiles during the pyrolysis of a solid fuel particle

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Abstract

The heating value of volatiles released from a solid fuel particle during pyrolysis is determined as a function of time. The experimental setup consists of a thermogravimetric analyser (TGA) and a flow-calorimeter (FC). One single fuel particle is quickly inserted into the TGA which is continuously purged with N_2 and operated at a constant temperature of 825 °C. The evolved volatiles are burnt in the FC with air while maintaining an excess of oxygen. The temperature change of the FC corresponds to the heat production rate (HPR) from combustion of the volatiles. The relation between temperature change and HPR is given by the convolution integral. The Hammerstein approach describes the non-linear response behaviour of the FC. The heating value of the volatiles is calculated from the HPR and the mass loss of the particle. The experimental setup was calibrated with C_3H_8 and applied to gas from the pyrolysis of a single dry beech wood cube (15 mm × 15 mm × 15 mm). It was found that the heating value of the released volatiles shows two maxima during the pyrolysis process.

Keywords: Heating value; Calorimeter; Volatiles; Fuels; Pyrolysis

1. Introduction

During the thermal decomposition of solid fuels, each fuel produces volatiles which consist of numerous components. Tar, a complex mixture of condensable hydrocarbons, represents the major part of the volatiles [1,2]. Because of the complexity of tar, the exact composition of the volatiles, as is their accurate chemical and physical properties, is unknown. A comprehensive description of combustion or gasification processes, however, requires that the properties of all volatiles be known. In particular, the modelling of transient conversion processes needs the heating value of the volatiles as a function of time.

Several methods are known to continuously determine the heating value of a gas [3–9]. An analysis of the gas composition and the subsequent calculation of the heating value is a common approach [3]. The total heating value results from the heating values of the different components and their concentrations in the gas-mixture. But this method is inconvenient for gas containing unidentified tar. The majority of the methods [4–9] are based on the combustion of the gas and the resulting effects such as a change in temperature. The combustion of gas can be achieved

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Nomenclature

E	unit-function (°C/W s)
H_i	heating value inferior (kJ/kg)
m	mass of fuel particle (kg)
m_d	mass of fuel particle related to its dry mass (−)
$\dot{m}_\mathrm{d}$	differential mass loss of fuel particle related to particle's dry mass (s^{-1})
n	number of data (−)
P_cnl	correction for non-linearity (W)
P_R	heat production rate, HPR (W)
P_Red	reduced heat production rate, RHPR (W)
t	time (s)

Greek symbols

Θ	temperature (°C)
$\Delta\Theta$	temperature change of the flow-calorimeter (°C)

Subscripts

air	combustion air
c	calculated
CM	catalyst-module
C1	middle of first catalyst
C1,i	entry of first catalyst
C1,2	interspace between first and second catalyst
C2	middle of second catalyst
C2,o	exit of second catalyst
FC	flow-calorimeter
FC,0	flow-calorimeter at the beginning of an experiment
gas	gas to be analysed
stp	standard temperature (0 °C) and pressure (1.013 bar)

either in a flame or in a catalyst. Devices such as a Cutler–Hammer calorimeter [4], Union-Schnellgeber [5] or Junkers-calorimeter [6] use a burner in order to oxidise the gas to be analysed. These devices are also not suitable for gas containing tar. The tar causes problems in the operation of the burner. The methods of Maeda [7], Goldberg [8] or Bohl et al. [9] apply a catalyst to burn the gas. This has the advantage that the catalyst converts gas at extremely low concentrations which may even be below the ignition limit of the gas. For the methods based on catalytic combustion [7–9], a gas flow is required which is either constant or adjustable. The flow of volatiles from a single fuel particle, however, is neither constant nor is it adjustable.

To measure the heating value of the unsteadily produced volatiles from one single "large" fuel particle, a thermogravimetric analyser (TGA) was combined with a flow-calorimeter (FC) the latter being based on catalytic combustion. Quick insertion of the particle into the TGA means that the heating conditions for the fuel particle are similar to those in large scale firings. The rise in temperature of the FC and the mass loss of the particle are used to determine the heating value of the complete volatiles as a function of time. The experiment, the handling of measured data and the heating value of volatiles from beech wood are all described bellow.

2. Experimental

2.1. Setup

The major parts of the experimental device are the TGA and the FC (see Fig. 1). The experimental setup also comprises a supply of purge gas, combustion air and calibration gas, a flame ionisation detector (FID) and a computer for data recording. The TGA consists of a muffle furnace (LINN-High-Therm, type VMK-S22) and a balance (METTLER, type PM 300). A sample basket is located inside the muffle furnace and is connected to the balance. The inner dimensions of the muffle are 100 mm × 90 mm × 140 mm. By means of a gas-tight sluice device and a sample-holder, fuel particles of up to 20 mm in diameter can quickly be placed on the sample basket. Inside the FC two monolithic catalysts (0.2 wt.% platinum on cordierite, provided by Chemisch Thermische Prozesstechnik (CTP), Graz, Austria) are arranged in series. Each catalyst has a diameter of 45 mm and a length of 100 mm with 62 channels/cm^2, the maximum allowable operating temperature is 830 °C. The catalysts are embedded in an insulation layer with a thickness of 20 mm, which is high-temperature resistant and gas-tight at its surface. Due to the insulation, the heat losses are negligible. Several thermocouples (THERMOCOAX, type K-TKA-05) are arranged in

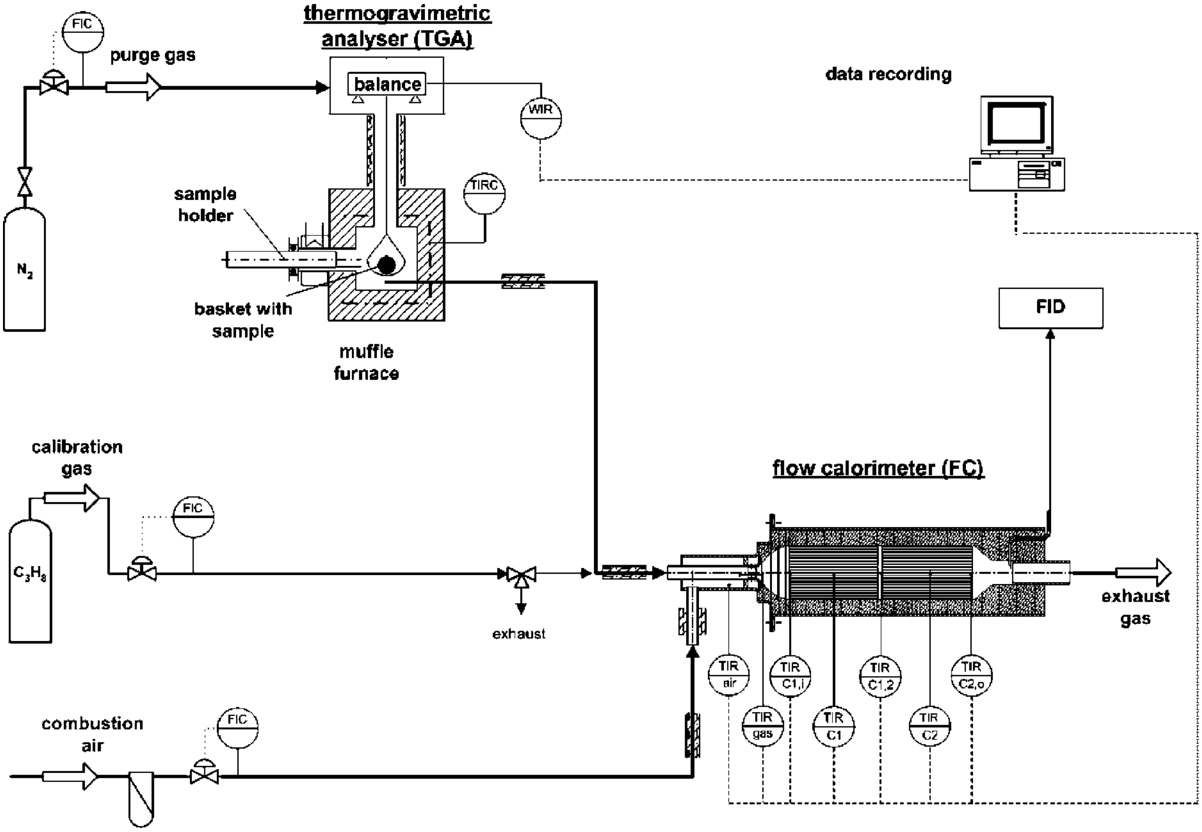

Fig. 1. Flow-sheet of the experimental setup.

the central along the axes inside the FC. Directly in front of the first catalyst, three fine wire meshes and a mixing nozzle enable a uniform distribution of the gas-flow across the catalyst's cross-section.

2.2. Procedure

The experimental device is operated in calibration mode or in measurement mode. In calibration mode, experiments are carried out with different flows of abrupt C_3H_8 feed into the experimental device; no fuel particles are placed in the TGA. C_3H_8 is chosen as calibration gas for both the FC and the FID. The muffle furnace is heated to a constant temperature of 825 °C and purged with a constant flow of 800 l/h_{stp} N_2. In the calibration mode, C_3H_8 is injected into the preheated N_2-flow behind the muffle furnace. Afterwards the N_2-flow transports the calibration gas into the FC. Inside the FC, C_3H_8 is mixed with preheated combustion air and burnt in the catalyst. To achieve complete combustion of C_3H_8, the FC is continuously heated to a temperature of 530 °C by both the purge gas and the combustion air. The flow rate of combustion air is kept at a constant level of 5570 l/h_{stp}. Calibrations are performed with constant flow rates of C_3H_8 in the range from 0.937 to 31.24 l/h_{stp}, which is equivalent to heat production rates (HPRs) from 23.8 to 792 W. The HPRs are based on an inferior heating value for C_3H_8 of 2044 kJ/mole [10]. The temperatures inside the FC as well as the C_3H_8-equivalent of the FID in the exhaust gas are measured continuously during each experiment.

In measurement mode, the operating conditions of the experimental device are equal to those of the calibration mode, i.e. constant purge of 800 l/h_{stp} N_2 through the TGA, constant temperature level of 825 °C in the muffle furnace, constant flow rate of 5570 l/h_{stp} combustion air and FC heated to 530 °C. No calibration gas is used. One single solid fuel particle is quickly placed on the sample basket of the balance. Due to the heat of the muffle furnace, volatiles evolve from the fuel particle. The N_2-flow purges the generated volatiles to the FC, where they are mixed with combustion air and burnt. The combustion of the volatiles takes place inside the catalyst in the presence of excess oxygen.

Volatiles from a dry beech wood cube with a size of 15 mm × 15 mm × 15 mm and a mass of 2.28 g are investigated. Throughout the whole pyrolysis process, the balance of the TGA detects the weight of the particle and thermocouples measure the temperature inside the FC. The FID measures the C_3H_8-equivalent of the organic carbon in the exhaust gas in order to monitor the complete combustion of the volatiles.

3. Results and discussion

The change in temperature of the FC, which corresponds to the HPR of the volatiles, and the mass-loss of the particle are required to determine the heating value of the released volatiles as a function of time. The heating value of the released volatiles H_i can be calculated by means of the following equation:

$$H_i(t) = \frac{P_R(t)}{dm(t)/dt} \quad (1)$$

where P_R is the HPR from combustion of the volatiles, and m is the mass of the particle at the current time t. The derivative with respect to time of the mass of the fuel particle is equivalent to the mass flow rate of the volatiles.

Since the mass of the particle is measured continuously, the derivative of the mass can easily be determined by differentiation. The determination of the HPR, however, is difficult because the catalyst temporarily stores heat. The heat is released again but distributed over time. Hence, the change in temperature of the FC occurs with a delay in time with regard to the combustion process. The correct values for the HPR of the volatiles can be determined by mathematical treatment of the measured change in temperature.

3.1. Determination of the HPR

A complex mathematical description of the processes inside the catalyst would consider the mass transfer to and from the reaction surface, the adsorption of reactants, the reaction itself and the desorption of products. A simpler method would be a transient energy balance for the FC assuming constant properties of gas inside the FC. The assumption is acceptable due to the high-dilution of the volatiles by the purge gas and the combustion air. Neither approach, however, is likely to succeed in determining of the HPR using the temperature change of the FC. This is for two reasons. First, the properties of the volatiles are unknown due to the high-content of tar. Second, the catalyst shows a shift in the spatial spread of the reaction zone inside the catalyst at different HPRs. Thus, different ranges of the catalyst, i.e. different masses, store energy.

A very promising approach is given by the convolution integral suggested by Hemminger and Höhne [11] and Levenspiel [12]. The convolution integral describes a mathematical relation between input- and output-signals of a system. In the case of the FC, the input-signal is represented by the HPR P_R and the output-signal corresponds to the temperature change $\Delta\Theta$ of the FC. Consequently, the convolution integral can be written as

$$\Delta\Theta(t) = \int_0^t P_R(\tau) E_{FC}(t-\tau)\,d\tau \quad (2)$$

The FC-function E_{FC} characterises the change of the input-signal due to the system, i.e. due to the FC. It is determined by calibration. In calibration, a defined flow of C_3H_8 is abruptly fed into the FC. Fig. 2 depicts the measured data of a calibration experiment with 6.25 l/h_{stp} (158 W) C_3H_8. Though the step input, the temperatures inside the FC rise with a time delay. The thermocouple at the end of the second catalyst reacts slowest.

In order to use the convolution integral, the signal transformation of the FC must exhibit linear behaviour, i.e. the temperature change $\Delta\Theta$ of the FC must be independent of the HPR. As a consequence, the temperature changes of different calibration experiments related to the respective HPR must be congruent. But this is not the case if the temperature at the end of the second catalyst $\Theta_{C2,0}$ or the temperature in the middle of the first catalyst Θ_{C1} is used to represent

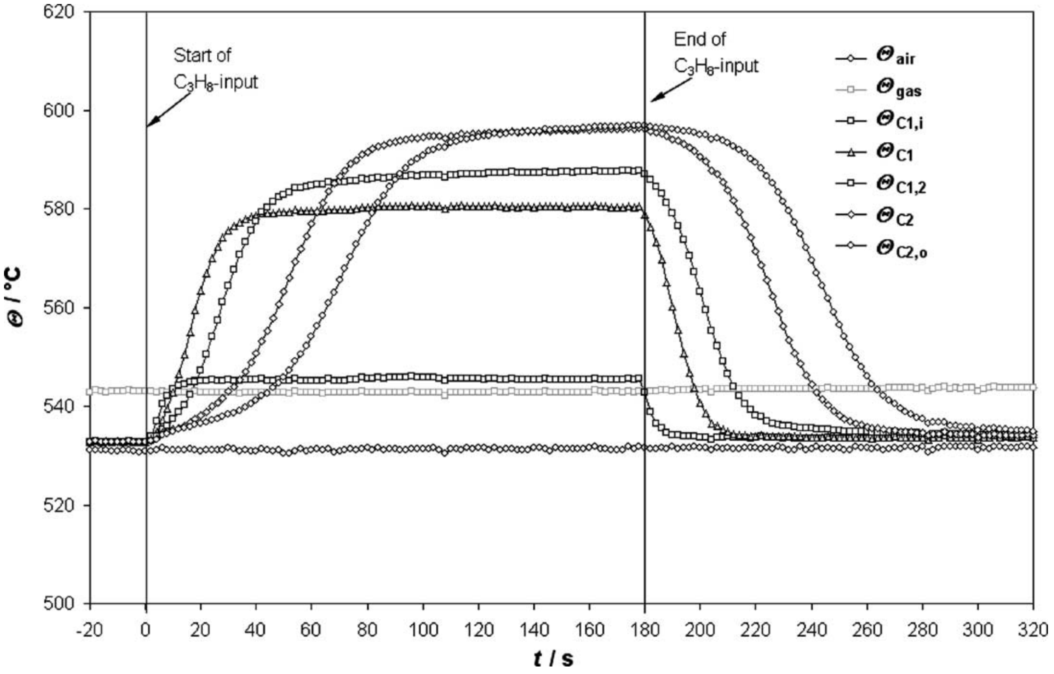

Fig. 2. Measured data of a calibration experiments (6.25 l/h_{stp} (158 W) C_3H_8).

the temperature change $\Delta\Theta$ of the FC. Conversion of the volatiles might also not be complete in the middle of the first catalyst, but this effect can be taken into account in the calibration of the FC.

Based on the temperature of the first catalyst, Fig. 3 demonstrates the temperature change $\Delta\Theta$ of the FC related to the HPR of different calibration experiments. Since the temperature of both gas flows into the FC is kept constant, the temperature change $\Delta\Theta$ of the FC is calculated by

$$\Delta\Theta(t) = \Theta_{\mathrm{C1}}(t) - \Theta_{\mathrm{FC,0}} \qquad (3)$$

where Θ_{C1} represents the temperature in the middle of the first catalyst, and $\Theta_{\mathrm{FC,0}}$ is the temperature of the FC at the beginning of an experiment. In Fig. 3, the curves do not cover each other. This characterises non-linear signal transformation of the FC and would exclude a solution using the convolution integral (2). However, the temperature change determined by the temperature in the middle of the first catalyst Θ_{C1} shows a static non-linear behaviour of the FC's signal transformation in contrast to the temperature change determined by the temperature at the end of the second catalyst $\Theta_{\mathrm{C2,0}}$. The static non-linear behaviour of the FC's signal transformation can be reduced to linear behaviour by means of the Hammerstein approach found in [13]. As a result, the approach based on the convolution integral (2) can be applied to determine the HPR.

3.1.1. *The Hammerstein approach*

This approach [13] describes a relation between input- and output-signal of static non-linear systems. It separates a system into a linear and a non-linear part. Applied to the FC, a fictitious division is made into a non-linear module and a catalyst module, the latter showing linear signal transformation. Fig. 4 illustrates the Hammerstein approach.

The HPR P_{R} (input-signal into the FC) is changed by the non-linear module. The result of this change is the reduced heat production rate (RHPR) P_{Red}. The RHPR causes a temperature change (output-signal from the FC) of the catalyst module which corresponds to the temperature change $\Delta\Theta$ of the FC. So, the measured temperature change $\Delta\Theta$ in relation to the RHPR results in a linear signal transformation. This enables the use of the convolution integral. The

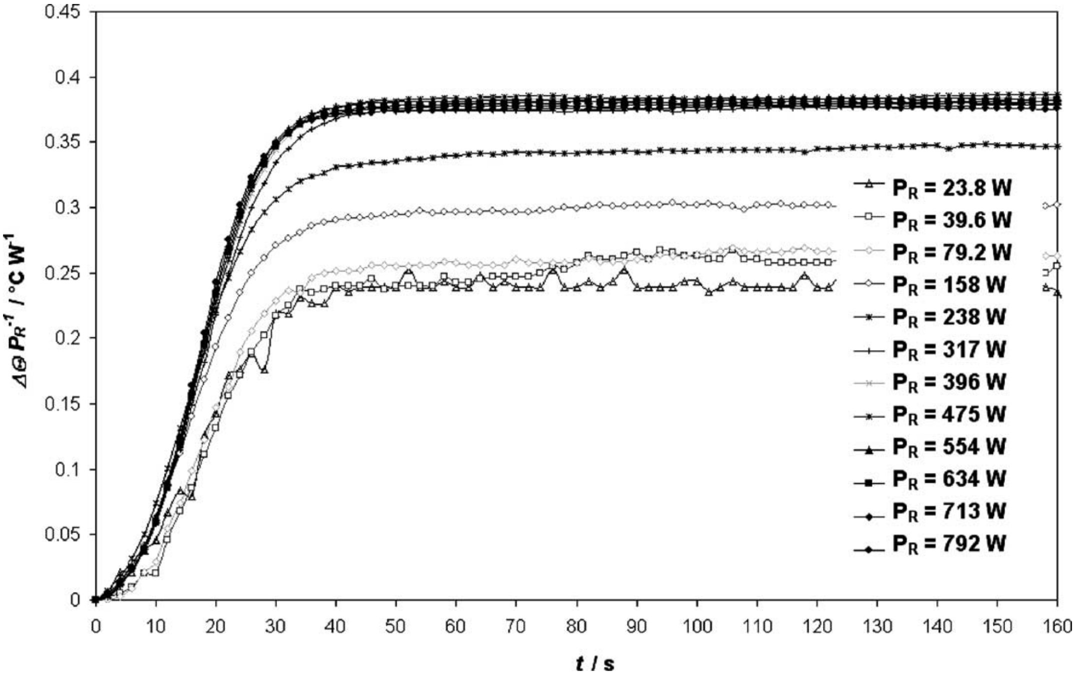

Fig. 3. Temperature change $\Delta\Theta$ of the FC in relation to the HPR P_R of C_3H_8 during calibration.

convolution integral can be written as

$$\Delta\Theta(t) = \int_0^t P_{\mathrm{Red}}(\tau) E_{\mathrm{CM}}(t-\tau)\,\mathrm{d}\tau \qquad (4)$$

3.1.1.1. Determination of the RHPR. The RHPR P_{Red} can be determined by means of the HPR and the temperature change $\Delta\Theta$ of the FC from calibration experiments. To get the values of the RHPR, the measured temperature changes $\Delta\Theta$ of the FC at a definite time are depicted in relation to the individual HPRs. Since the FC shows a static non-linear behaviour, the temperature changes $\Delta\Theta$ can be taken at any time of the experiment. The only restriction is that it has to be the same time for all calibration experiments. For stationary conditions of the FC, Fig. 5 shows the measured temperature change $\Delta\Theta$ of the FC from calibration experiments depending on the HPR.

A deviation from linear behaviour can be seen at low values of the HPR. In Fig. 5 the determination of the RHPR is exemplary. The RHPR is that quantity which yields the same temperature change $\Delta\Theta$ as the HPR which prevails during the calibration experiment. Using this relation, each value of the HPR results in a definite RHPR. The difference between the HPR and the RHPR is the correction of non-linearity P_{cnl}. The correction of non-linearity P_{cnl} is required to calculate the HPR for experiments in measurement mode.

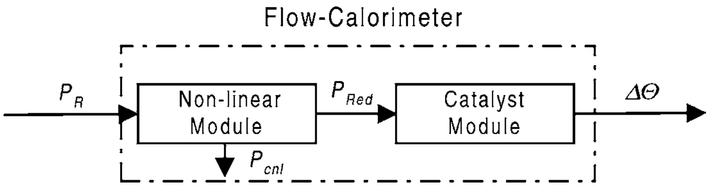

Fig. 4. The Hammerstein approach.

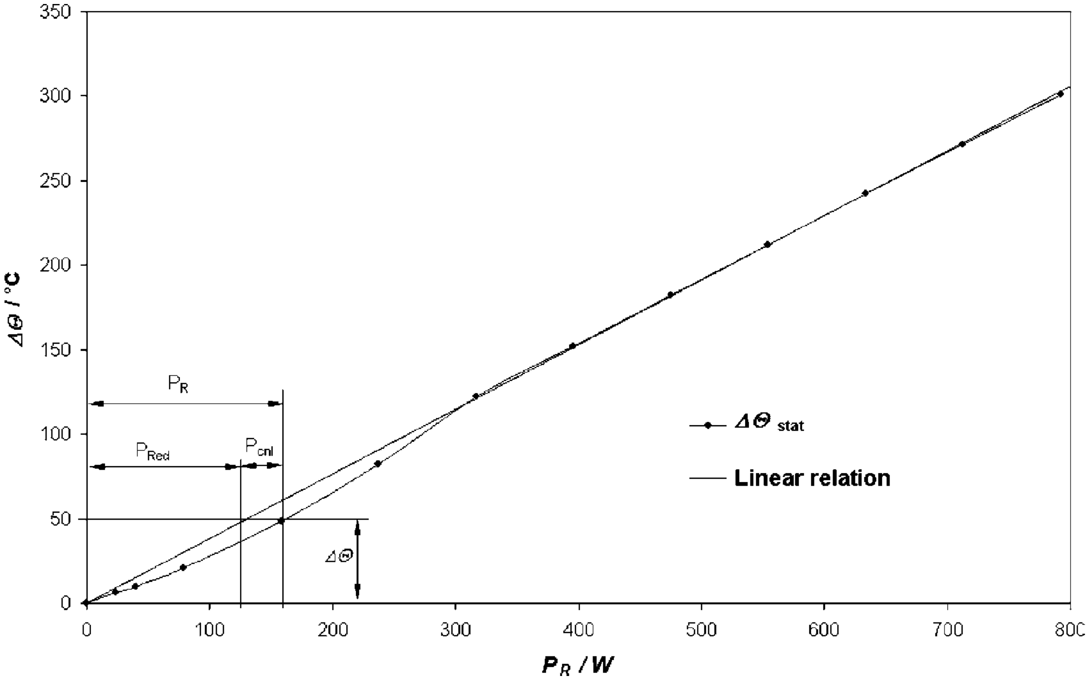

Fig. 5. Temperature change $\Delta\Theta$ of the FC under stationary conditions.

3.1.1.2. Determination of the catalyst-module-function (E_{CM}). Since the RHPR of each calibration experiment is known, the E_{CM} can be determined. For this purpose, the temperature change $\Delta\Theta$ is related to the RHPR. The result is a standardised output which is illustrated in Fig. 6. The curves of the different calibration experiments largely match each other. The overlap of the curves characterises signal transformation with linear behaviour.

As described in Levenspiel [12], the E_{CM} results from the derivative of the standardised output. It is given by

$$E_{\mathrm{CM}}(t) = \frac{\mathrm{d}(\Delta\Theta(t)/P_{\mathrm{Red}})}{\mathrm{d}t} \tag{5}$$

Fig. 7 shows the standardised output which is represented by the mean of all calibration experiments. Its derivative is the E_{CM}.

Based on the E_{CM} and the convolution integral (4), the RHPR can be calculated by means of the temperature change $\Delta\Theta$ of the FC. On taking the correction of non-linearity P_{cnl} into account, the result is the HPR as a function of time.

3.2. Heating value of volatiles from beech wood

The determination of the heating value H_i of unknown volatiles is demonstrated with the experimental data recorded for the beech wood particle. The temperature change $\Delta\Theta$ of the FC corresponds to the HPR based on the Hammerstein approach. Both the HPR and the mass loss of the particle are necessary to determine the heating value of the volatiles.

Fig. 8 shows the measured temperature change $\Delta\Theta$ of the FC and the relative mass of the beech wood particle related to its dry weight m_{d}. After approximately 100 s the mass of the particle does not change any more. While this indicates the end of the pyrolysis process, temperature changes inside the FC still occur.

In order to determine the HPR, the convolution integral (4) has to be solved for the RHPR. The most frequent methods used for this mathematical operation are Laplace-, Fourier-, or Z-transformations. But all of these have difficulties in handling the recorded data, for example in identifying transformable functions, in the generation of oscillations or in restricting to polynomials. Therefore, an iterative method was chosen

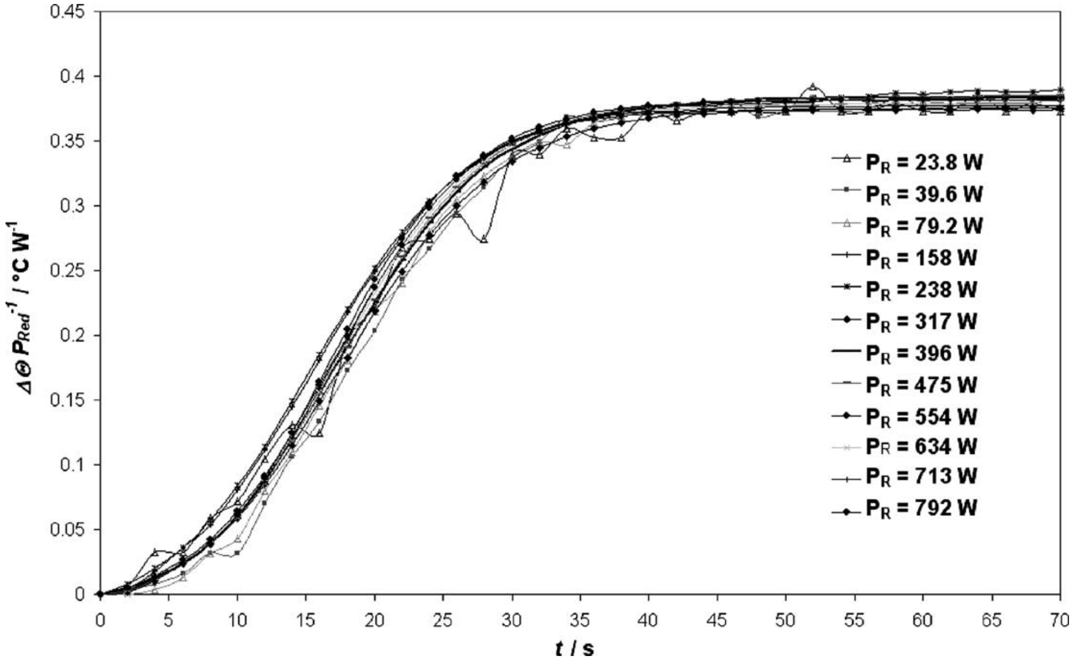

Fig. 6. Standardised output of the catalyst module.

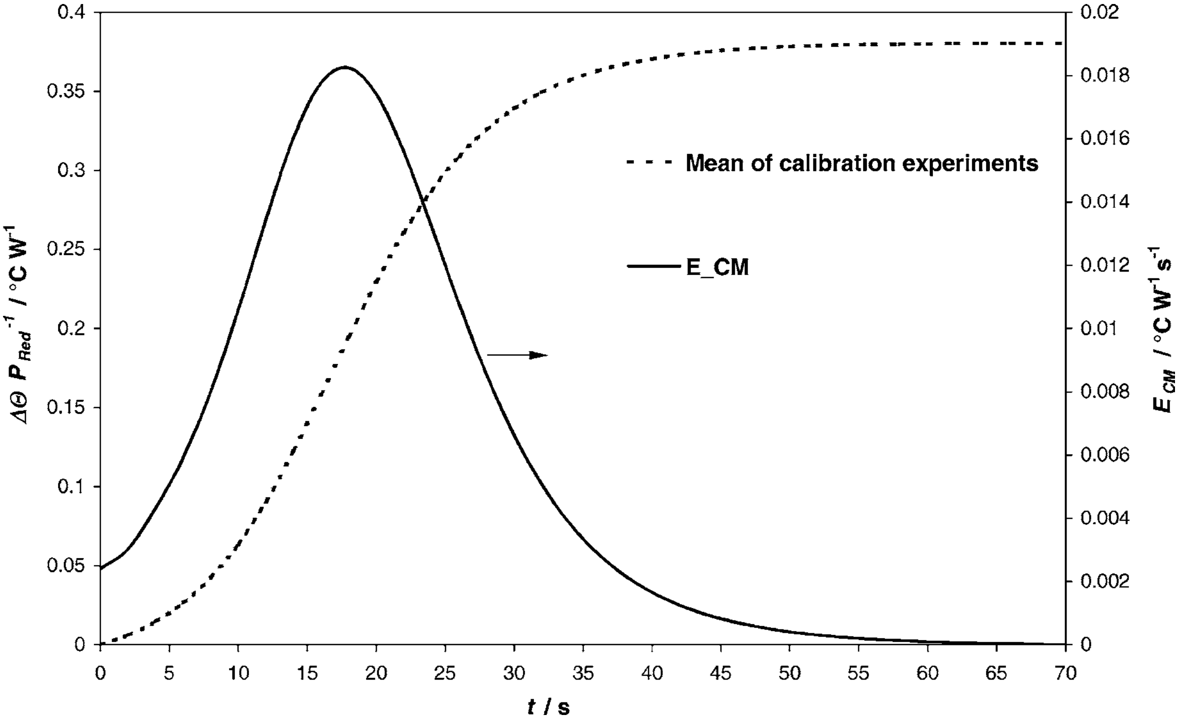

Fig. 7. The catalyst-module-function E_{CM}.

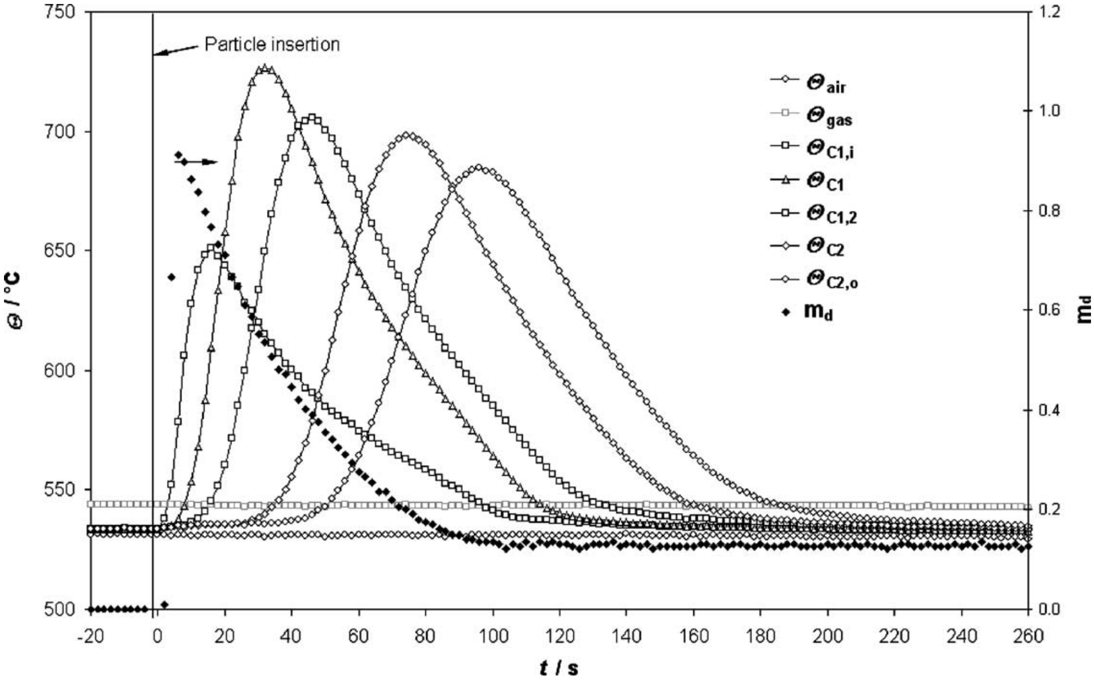

Fig. 8. Results of the experiment with beech wood; dry cube (15 mm × 15 mm × 15 mm) quickly inserted into the TGA (constant 825 °C, purge N_2 800 l/h_{stp}), evolved volatiles burnt in the FC (combustion air 5570 l/h_{stp}, 530 °C at start).

to help determine the RHPR from the experimental data.

The RHPR is calculated iteratively. In a first step, values for the RHPR are assumed. At the beginning of the iteration, the values for the RHPR are zero. Using the E_{CM}, the assumed values of the RHPR are used in a second step to calculate an approximation of the temperature change $\Delta\Theta_{\mathrm{c}}$. Analogous to Eq. (4) we can write

$$\Delta\Theta_{\mathrm{c}}(t) = \int_0^t P_{\mathrm{Red}}(\tau) E_{\mathrm{CM}}(t-\tau)\,\mathrm{d}\tau \qquad (6)$$

The approximation of the temperature change $\Delta\Theta_{\mathrm{c}}$ is compared to the measured temperature change $\Delta\Theta$. By means of the least-square method, the values for the RHPR are optimised until the difference between measured $\Delta\Theta$ and calculated temperature change $\Delta\Theta_{\mathrm{c}}$ of the FC is below a certain margin of error. This is calculated according to the following expression, where n is the number of data elements:

$$\frac{\sum_{j=1}^{n}(\Delta\Theta_{\mathrm{c},j} - \Delta\Theta_j)^2}{n} < 1 \qquad (7)$$

The error value of "1" is relatively large in order to avoid oscillations in the RHPR. The whole procedure of the iteration is done by MS-EXCEL and its integrated Solver. With a Pentium® II 300 MHz processor, and for 100 data points, the iteration is completed after approximately 7 min. Fig. 9 presents the final results of the iteration. The calculated temperature change $\Delta\Theta_{\mathrm{c}}$, which results from the RHPR, agrees very well with the measured temperature change $\Delta\Theta$.

The correction for non-linearity P_{cnl} is added to the RHPR, which results in the HPR of the volatiles. Fig. 10 shows the HPR of the volatiles, the RHPR and the correction for non-linearity P_{cnl}. The major part of the HPR results from the RHPR. The correction of non-linearity is of a minor order of magnitude in comparison to the RHPR.

The mass flow of the volatiles is also required to determine the heating value H_i of the volatiles. The mass flow of the volatiles is equivalent to the differential mass loss of the wood particle given by differentiating the measured mass signal with respect to time. Fig. 11 depicts the mass of the particle after its insertion into

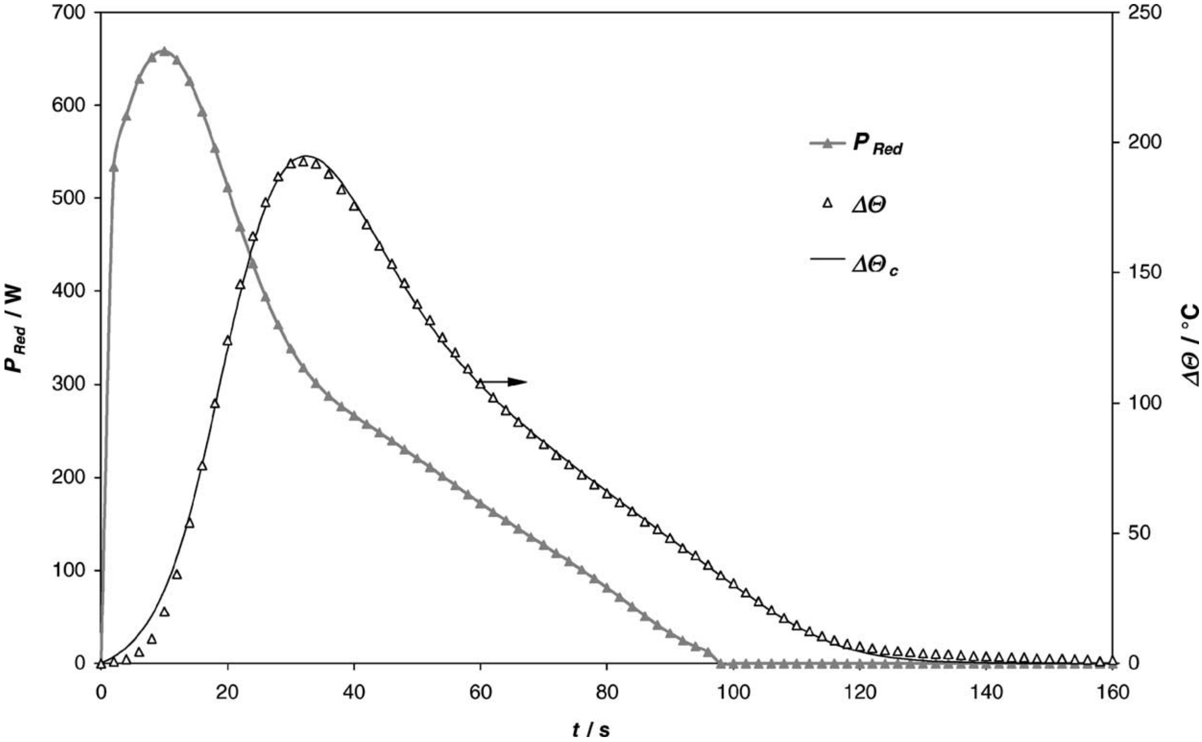

Fig. 9. Final result of iteration.

the muffle furnace. The mass of the particle is related to the mass of the dry particle. Since the particle releases volatiles before the particle can be placed on the sample basket of the balance, a fit function is applied to describe the relative mass of the particle m_{d}. The fit function starts with the value "1" at the beginning of the pyrolysis process, since the mass of the dry particle is known from weighing on a lab-balance. The fit function is also used to calculate the differential mass loss. To skip numerical problems in the determination of the heating value, the differential mass loss is presumed to be zero as soon as the change of the particle's mass is within the accuracy-limit of the balance. Finally, the heating value H_i of the volatiles as a function of time results from the division of the HPR by the differential mass loss according to Eq. (1).

Fig. 12 shows the heating value H_i of the volatiles from the beech wood particle (15 mm × 15 mm × 15 mm) as a function of time. The figure also depicts the HPR of the volatiles P_{R} and the differential mass loss of the particle, this latter corresponding to the mass flow rate of the volatiles.

The release of the volatiles is driven by the heat transfer to the particle. At the beginning of the pyrolysis process a lot of fuel mass—a high amount of volatiles—is released because outer shells of the particle, which have higher mass than inside shells, pyrolyse first. The gradual decrease after the maximum results from the limitation of the heat transfer inside the particle. Increasing distance for the heat transfer into the fuel particle and escaping volatiles from the inner, "cold" particle cooling the fuel particle decelerate the pyrolysis process [14].

The HPR demonstrates a tendency similar to the mass flow rate of the volatiles. The high release of the volatiles can also be seen in the high HPR at the beginning of the pyrolysis process. The HPR shows a maximum which corresponds to the maximum in the curve of the mass flow rate of the volatiles. The

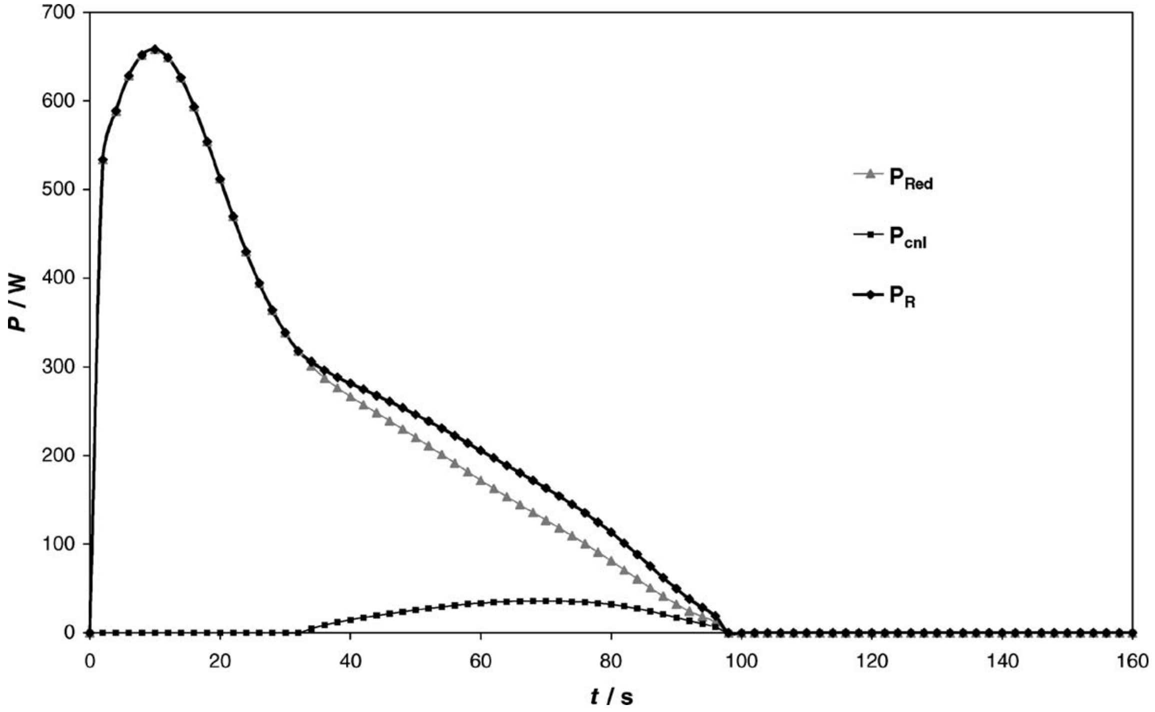

Fig. 10. HPR P_R of the volatiles from the beech wood particle.

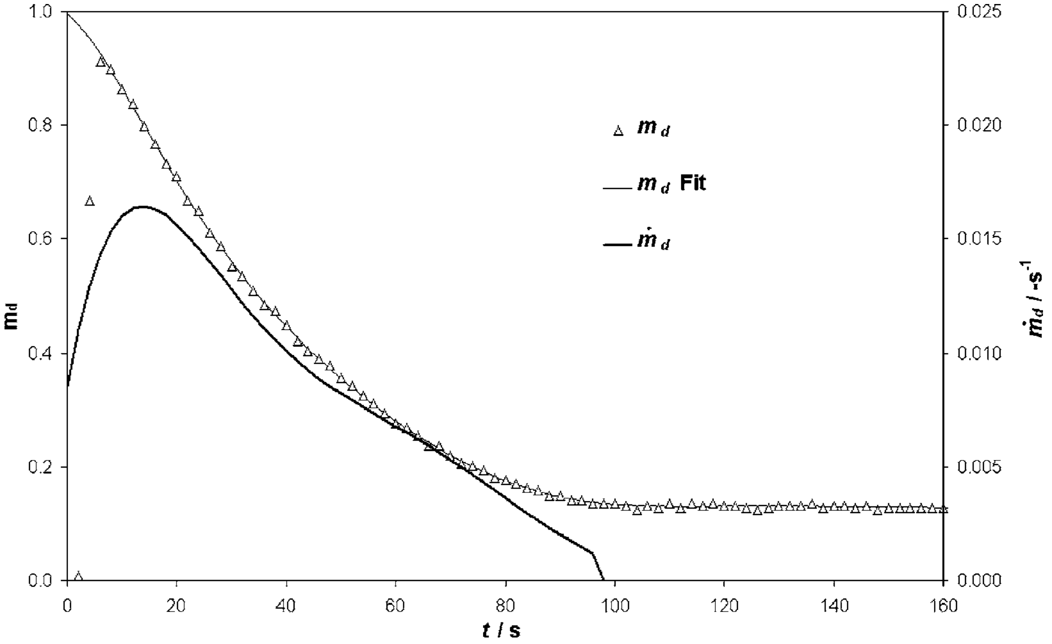

Fig. 11. Mass loss of the beech wood particle; dry cube (15 mm × 15 mm × 15 mm) quickly inserted into the TGA (constant 825 °C, purge N_2 800 l/h_{stp}).

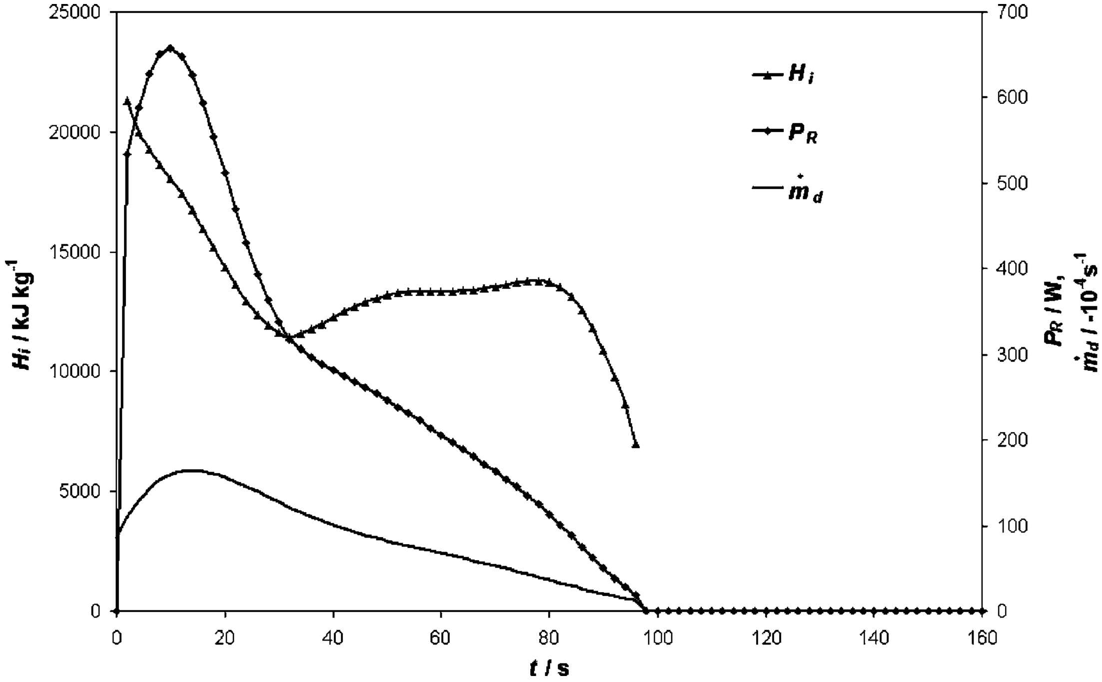

Fig. 12. Heating value H_i, HPR P_R and relative mass flow rate of the volatiles from the dry beech wood particle.

integration of the HPR results in the released energy Q of the volatiles. It is given by

$$Q = \int P_R \, dt \tag{8}$$

For the measurement results of the dry beech wood cube the released energy of the volatiles amounts to 28.9 kJ as calculated by Eq. (8). Neglecting the heat of pyrolysis [15], the released energy of the beech wood particle can also be calculated by

$$Q = H_{i,\text{wood}} m_{\text{wood}} - H_{i,\text{char}} m_{\text{char}} \tag{9}$$

Using the mass of the dry beech wood particle $m_{\text{wood}} = 2.28$ g, the mass of the char remaining after pyrolysis $m_{\text{char}} = 0.36$ g, the heating value of dry beech wood $H_{i,\text{wood}} = 18\,200$ kJ/kg and the heating value of the formed char $H_{i,\text{char}} = 33\,600$ kJ/kg (the heating values were determined by "Prüflabor Voitsberg" of Verbund, Austria), the released energy as calculated by Eq. (9) is 29.4 kJ. This result agrees very well with the released energy determined by the FC. So the conversion behaviour of different gas components inside the catalyst is perfectly represented by C_3H_8.

The heating value H_i of the volatiles describes the energy content of the volatiles. In Fig. 12, a quick comparison of the mass flow rate and the HPR would assume a constant value for the heating value. In fact, however, the heating value of the volatiles is not constant; it shows two maxima. One maximum can be found at the beginning and the other at the end of the pyrolysis process. As a result, the changes in heating values prove the existence of changes in the composition of the volatiles.

4. Conclusions

The combination of the TGA and the FC enables the determination of the heating value of all volatiles from a solid fuel at any time of the fuel's pyrolysis process. The heating value of the volatiles results from the mass loss of the fuel particle and the HPR of the volatiles during their combustion. The HPR of the volatiles is derived from the temperature change of the FC using the Hammerstein approach and the convolution integral. The FC is calibrated with C_3H_8

which perfectly represents the volatiles. As determined by the FC, the energy released during combustion of the volatiles from beech wood agrees very well with the difference in the energy content of the fuel and of the char. The heating value of the volatiles from beech wood shows two maxima during the process of pyrolysis.

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