Correction of the sample temperature in the thermal analysis chamber for studying the kinetics of carbon oxidation

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Abstract. This paper proposes a method for correcting the sample temperature under experimental conditions in the STA449F1 thermal analysis chamber. Carbon samples are oxidized in air-argon mixture, calorimetric signal is recorded and then processed to study the nutual interactions of heat transfer and chemical reaction. The technique is based on selecting the coefficients of the kinetic model and assessing its correctness using the simplest statistical metric.

1 Introduction

Thermogravimetry is one of the methods for studying the thermophysical and reactive properties of substances, including energy fuels. In a thermal analysis device, the sample is subjected to a given temperature effect, which is set through heating the walls of the chamber and the flowing gas mixture. At the same time, changes in its mass and other characteristics available for measurement (composition of products, thermal effects) are recorded.

When studying the processes of oxidation and decomposition of materials, accompanied by intense heat release, the crucible can be subject to significant overheating in comparison with the surrounding gaseous environment [1, 2]. For example, this manifests itself when studying fuel samples in an oxidizing atmosphere, when the temperature in the combustion zone differs from the specified program. Under certain conditions, overheating can lead to uncontrolled development of a chemical reaction [3]. In this case, the measured data (Fig. 1 and 2) need to be corrected.

In the paper [4], a technique was proposed for adjusting the sample temperature for endothermic processes (drying and evaporation of water). It was shown that the temperature difference between the sample surface and the gaseous environment can reach several tens of degrees (due to evaporative cooling). For correction, a calorimetric signal is required that registers the thermal potential difference between the reference crucible and the crucible containing the test sample. Processing this signal makes it possible to estimate the deviation of the sample temperature from the specified program. The inverse problem becomes more complicated, since both the reactivity of the sample and its thermophysical properties are usually unknown.

For simplicity, the work considers the oxidation of carbonaceous materials, which eliminates multi-stage reactions and narrows the range of expected thermal effects.

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2 Methodology

2.1 Initial data

The sample is placed in a 163 mg corundum crucible in a STA449F1 installation (High-Temperature Circuit Multi-Access Research Center) and is heated at a given speed. Crucible diameter 5 mm, height 4 mm, wall thickness 1 mm. The air-argon mixture flows from below. In these conditions, the mass loss of the sample and the DSC signal are recorded.

Figures 1 and 2 present the data obtained in the experiment.

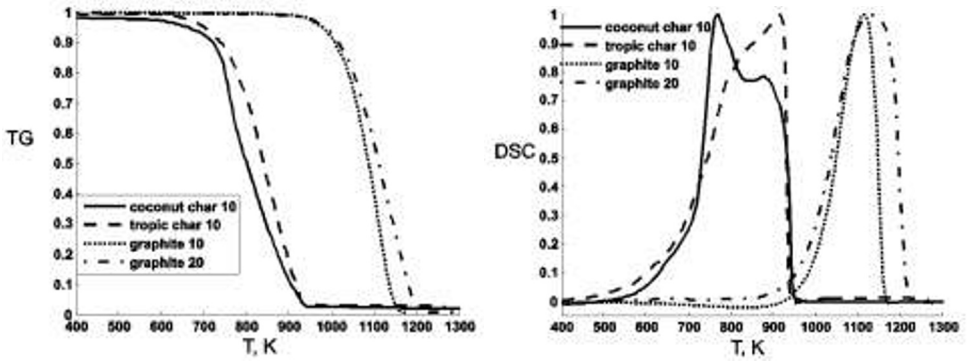


Fig. 1. Thermogravimetric and calorimetric oxidation curves of different types of carbon.

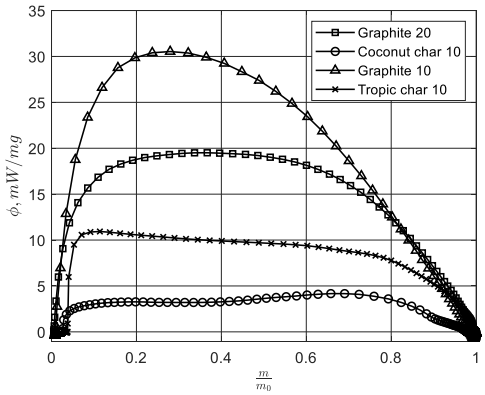


Fig. 2. DSC signal vs TG signal.

Table 1 shows the experimental conditions. The samples used are technical graphite and biofuel chars obtained by heating at a temperature of 800°C for 30 minutes. The samples were powdered up to the size of about 100 microns.

Table 1. Experimental conditions.

Sample name	Mass, mg	Heat rate, K/min	Flow rate, ml/min
Graphite 10	9.2	10	Ar 14 + Air 35

Graphite 20	9.5	20	Ar 14 + Air 35
Coconut char 10	36.9	10	Ar 20 + Air 70
Tropic char 10	25.2	10	Ar 20 + Air 70

2.2 Kinetic model

In the simplest case, the rate of a heterogeneous reaction is proportional to the surface area and the concentration of the gaseous reactant. The dependence of the reaction surface on the conversion degree (mass) is determined by the shape of the particles and their porosity. In the general case, such a dependence can be taken in the form of a power function with exponent n of the order of unity [5].

The equation for the rate of mass loss under the selected assumptions is as follows:

$$\frac{dm}{d\tau} = -S_0 \left(\frac{m}{m_0} \right)^n C_{O_2} A \exp\left(-\frac{E_a}{RT} \right), \quad (1)$$

where m is sample mass as a function of time, kg; C_{O_2} is oxygen concentration in the stream; τ is time, s; A is pre-exponential factor, mole·m^3·s^{-1} ; E_a is activation energy, J/mol; R is universal gas constant, J·K^{-1}·mol^{-1}; T is temperature, K.

The temperature in the sample T differs from the temperature in the chamber T_g. In order to take this into account, a transformation was made in equation (1): $T = T_g + k\varphi$, where φ is the registered DSC signal. Then equation (1) can be linearized in the following form:

$$\ln\left[-\frac{1}{m^n C_{O_2}} \frac{dm}{d\tau} \right] = -\frac{E_a}{R} \left(\frac{1}{T_g + k\varphi} \right) + \ln \bar{A} \quad (2)$$

Here $\bar{A}$ is pre-exponent multiplied by the specific surface area of the powder. The coefficients n and k are model parameters that need to be selected in the same way as the Arrhenius parameters.

For this purpose, the values n and k were varied: n = [0…1], k = [0…30]. For each combination the corresponding values of E_a and $\ln \bar{A}$ were found. To assess the correctness of the model, the simplest metric is used – the correlation coefficient.

An analysis of the literature data shows that the expected values of the activation energy for the carbon oxidation reaction lie in the range from 40 to 120 kJ/mol. All other things being equal, preference should be given to the coefficients n and k, at which the found activation energy falls within the specified range: graphite is a less reactive fuel, so the range for the activation energy shifts towards larger values; biofuel chars are more reactive fuels, so the activation energies are in the range of lower values (it can be assumed that the oxidation of biochars occurs in the intradiffusion conditions [5]).

3 Results

This section presents the results of calculations made using experimental data: the DSC signal φ and the sample mass loss m.

The markers on figure 3 mark the data that corresponds to the maximum absolute value of correlation coefficient in equation (2) for activation energy values equal to 100 and 50 kJ/mol for graphites and chars, respectively.

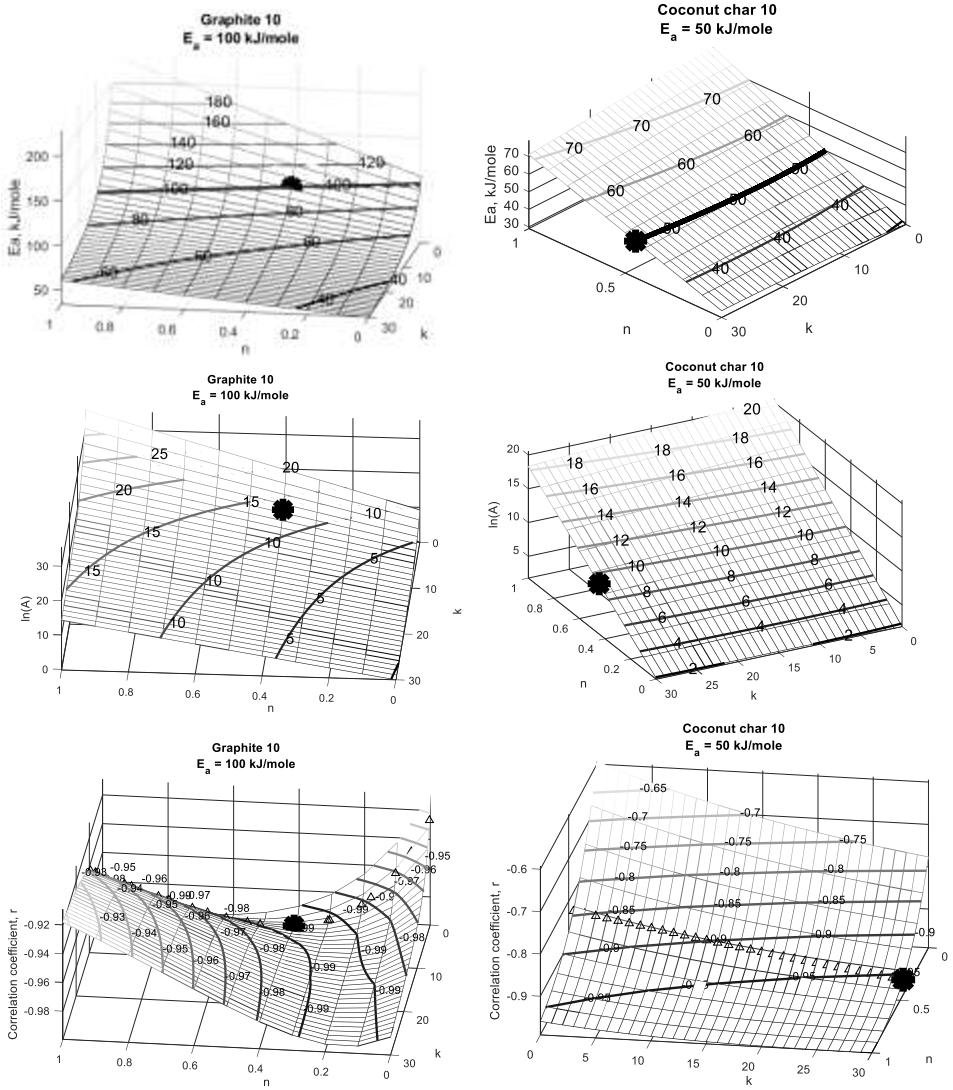


Fig. 3. Dependence of the activation energy values, the value $\ln A$ and the absolute value of the correlation coefficient on *n* and *k* for a graphite sample (left) and coconut char (right) (heating rate 10 K/min). The triangles indicate the values for the isolines equal to 100 and 50 kJ/mol for graphite and char, respectively.

Figure 3 shows that the activation energy value can vary from 30 to 200 kJ/mol for graphite and from 30 to 80 kJ/mol for coconut char.

Figure 4 on the left shows the curves of the dependences $\ln\left[-\frac{1}{m^n C_{O_2}}\frac{dm}{d\tau}\right]$ on $\frac{1}{T_g + k\varphi}$ for energy values equal to 100 and 50 kJ/mol for graphite and cinder, respectively. On the right is a comparison of the recorded and calculated temperature curves.

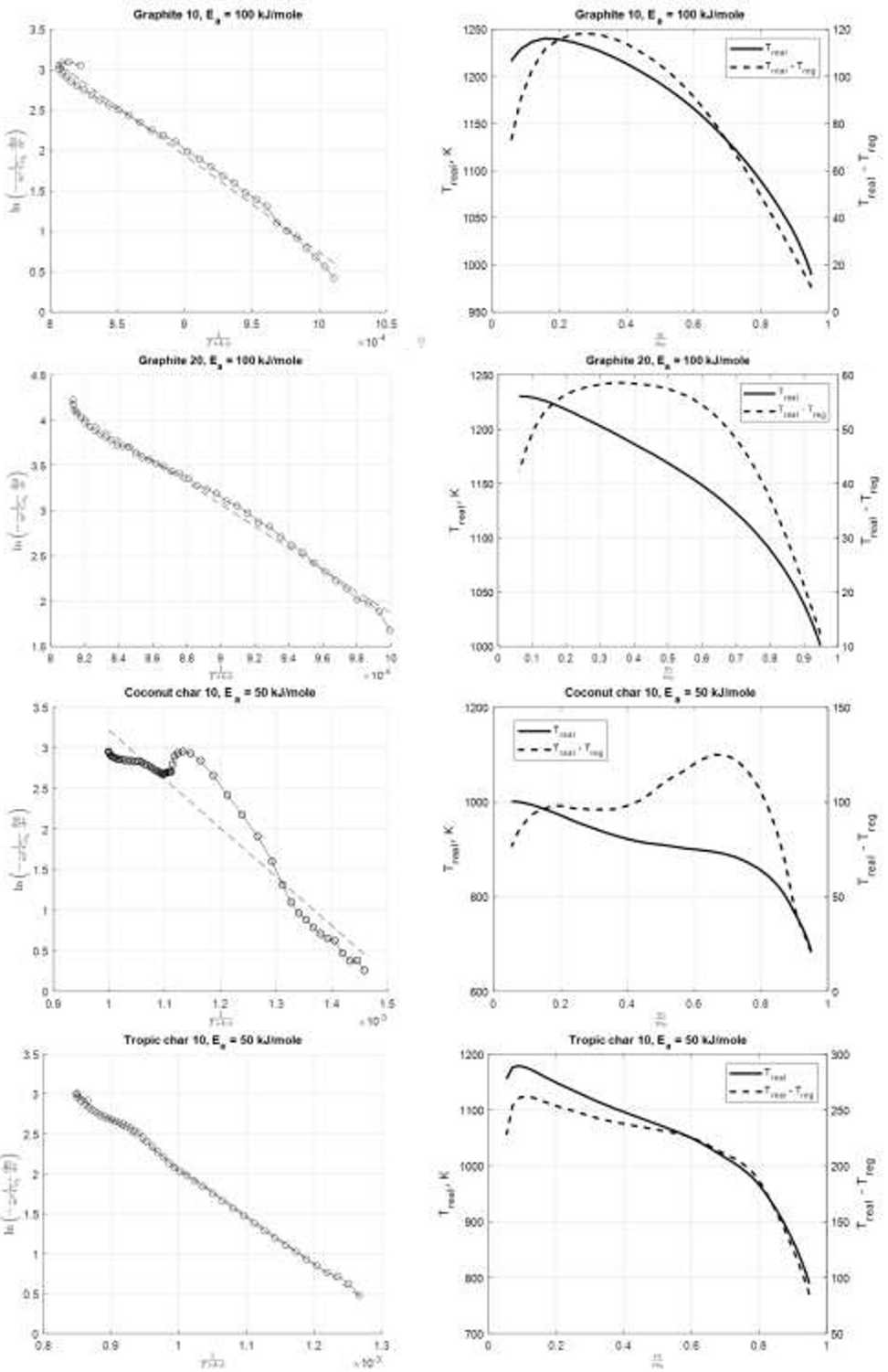
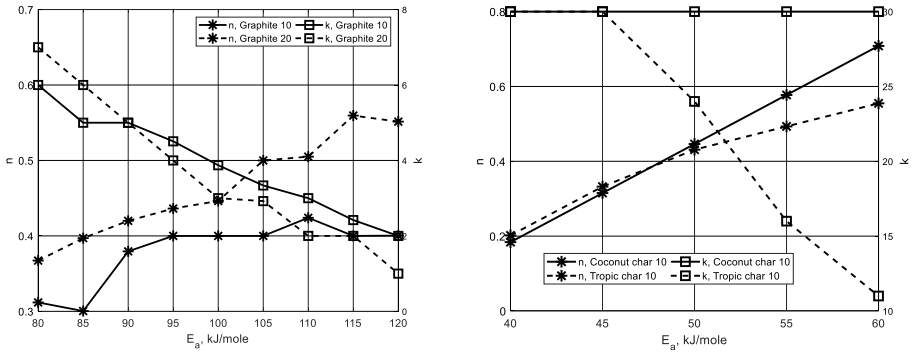


Fig. 4. Linear correlations and the corresponding difference between calculated and measured temperatures.

As can be seen from Figure 4, the maximum temperature difference between the sample and the reference crucible can reach 100-250 K. Such a large discrepancy can be the result of several factors. Firstly, the development of an exothermic reaction (especially for highly reactive biofuels) leads to significant overheating of the sample. In this case, generally speaking, transition from the kinetic regime to the diffusion regime may occur (such a transition is not taken into account in the model). Secondly, during the burnout process, the intensity of heat exchange between the sample and the thermal analysis chamber may change, both due to convective effects (Stefan flow, natural convection) and due to an increase in the radiative heat loss fraction. For more accurate estimates, it is necessary to develop a model of heat transfer in a crucible [6, 7]. Finally, the chosen metric (correlation coefficient) may be inadequate for the problem being solved: in this case, it is necessary to analyze different statistical metrics.

Figure 5 shows the dependence of the coefficients n and k on the activation energy corresponding to the maximum absolute correlation coefficient in equation (2).



a) b)

Fig. 5. Dependence of the calculated values n and k for the maximum correlation coefficient on energy values for a) graphite; b) coconut char.

4 Conclusion

This work proposes a new technique for processing thermogravimetry and differential scanning calorimetry signals to correct measurements taking into account an exothermic chemical reaction (carbon oxidation). Using a simple kinetic model, the temperature difference between the sample and the environment is estimated, and it is shown that this difference can reach hundreds of degrees. Possible sources of errors in the proposed methodology are discussed.

The results of this work can be used in the correction and statistical processing of the results of kinetic measurements.

The research was funded by the Russian Science Foundation, Grant No. 23-29-00406 (https://rscf.ru/project/23-29-00406/)

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