SELF-IGNITION OF COMBUSTIBLE BULK MATERIALS UNDER VARIOUS AMBIENT CONDITIONS

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It has been known for a long time that combustible bulk materials may undergo self-ignition if stored in sufficient amounts at adequate ambient temperatures. Most of the studies according to this problem refer to atmospheric ambient conditions (oxygen volume fraction of 21 %). In some technical applications, however, bulk materials are processed or stored at a reduced level of oxygen concentration. Besides the oxygen volume fraction, the moisture content of the bulk material itself as well as the humidity of the ambient air effect self-ignition.

The current paper presents experimental investigations on the influence of the volume fraction of oxygen on the self-ignition temperature of the bulk materials. The lower the oxygen volume fraction in the surrounding gas, the higher is the self-ignition temperature as a general trend. Furthermore, tests on this topic showed that sub-critical deposits of bulk materials could become super-critical by pouring water into the bulk or by exposing a dry bulk sample to humid air.

Besides the experiments, a numerical model was established which allows to compute the process of heating and self-ignition in bulk deposits. Technical applications of the model cover safe storage of dusts, granulate, bulk materials and wastes.

INTRODUCTION

Smouldering fires arising from self-ignition represent a serious exposure for man, environment and industry. Many factors influence the self-ignition process and are presented elsewhere [1], [2]: particle size, volume-to-surface ratio (V/A), porosity, thermal conductivity, density and heat capacity and convection in the surrounding. Nevertheless, some influences on this topic are still not sufficiently investigated, such as oxygen content in the surrounding, heat of wetting, condensation and evaporation of water inside the bulk material.

The current paper describes the experimental investigations to determine the influence of

- the oxygen concentration in the surrounding of the bulk material
- moistening of bulk material
- the ambient humidity

on the self-ignition of combustible dusts.

To avoid any kind of smouldering fire in the process industries, it is common to reduce the oxygen content in the surroundings of the stored bulk materials or dusts.

In the case of reducing process costs, it is important to know how the self-ignition temp-
erature (SIT) of the stored material depends on the oxygen content in the surrounding.

Another interesting effect on the self-ignition of combustible materials is brought
out by water. It is well known, that in some cases the temperature in the bulk phase
increases as a result of the generated "heat of wetting" and heat of condensation [3].
Pouring water on the material generates an additional heat in the bulk phase, while expos-
ing the specimen to a high ambient humidity leads to a total heat generation consisting of
condensation and wetting. These effects can turn a sub-critical into a super-critical deposit
of a combustible material. As a result of the temperature rise in the bulk phase an ignition
cannot be excluded.

EXPERIMENTAL SETUP

The experiments were carried out for German lignite coal consisting of two particle size
fractions (detailed information in appendix Table 1).

The experimental setup for the determination of the self-ignition temperatures with
a reduced oxygen content in the surrounding is presented in Figure 1.

A chamber was installed inside of a regular heat storage oven to adjust a defined
oxygen content in the surrounding of the specimen. This chamber was flushed afterwards
with an air-nitrogen mixture of the desired concentration. The mixture flow (100 l/h) was
measured continuously with a flowmeter and was preheated with a copper pipe coil before
entering the inner chamber. To replace the air inside of the voids of the specimen, the
sample was evacuated with a vacuum-drier and then flushed with the air-nitrogen
mixture before the measurement. During the experiment, the oxygen content in the
surrounding of the specimen was measured continuously with an oxygen analyzer.

These experiments were carried out for German lignite coal fraction A and B.
According to [4], equidistant cylindrical baskets with volumes of 31, 100, 400, 800,

Table 1. Particle size distribution of German lignite coal in %

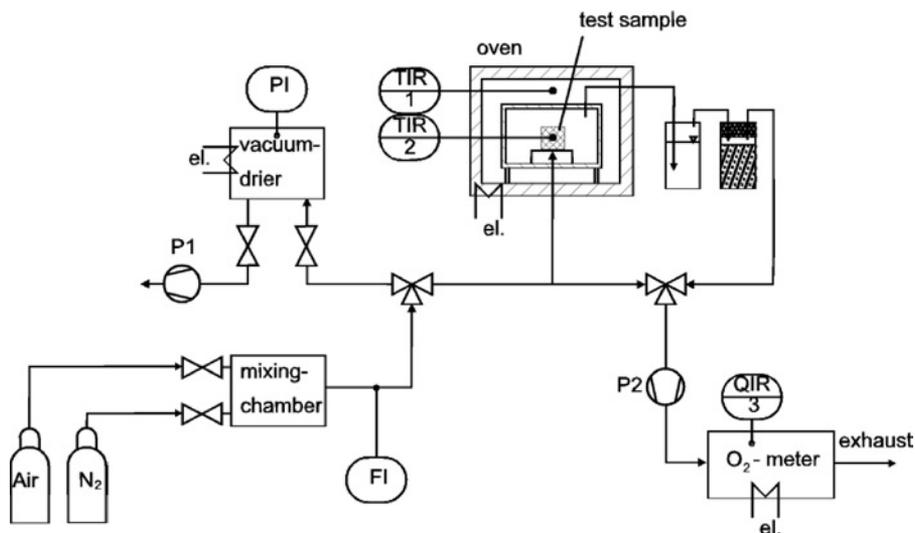| Particle fraction in μm	Lignite coal (fraction A)	Lignite coal (fraction B)
<20	25,3	–
20–40	20,7	–
40–63	18	–
63–125	20	–
125–200	11	9,8
200–315	5	4,3
315–500	–	2,4
500–1000	–	10,1
1000–2000	–	60

Figure 1. Experimental setup for the determination of the self-ignition temperatures with a reduced oxygen content in the surrounding

3200, 6400 and 12800 ml were used. The SIT was determined for oxygen concentrations of 21, 16, 12, 6, 3 and 1,3 %.

The experiments to determine the influence of wetting on the SIT were carried out for German lignite coal fraction B, with equidistant cylindrical baskets of 3200 and 6400 ml and 21 % of oxygen in the surrounding. The specimen were placed in a heat storage oven and stored at a temperature below its SIT. As soon as the temperature in the middle of the specimen reached its maximum, the oven was opened and 1000 ml of water were poured on the surface of the bulk material. The temperature of the added water was always equal to the oven temperature. The procedure was carried out for various oven temperatures.

Preliminary tests to determine the quantity of the heat of wetting were carried out for lignite coal fraction A. For these experiments, the influence of the initial water content in the material and the amount of added water on the heat of wetting was investigated. A coal sample of 0,1 kg was placed in a Dewar-container and water was poured on the surface. After mixing the coal with the added water for app. 60 seconds, a temperature rise (ΔT) in the middle of the specimen was determined. The temperature in the mixture reached a constant level after a certain time and the heat of wetting (Q) could be calculated with eq. (1):

$$Q = ([m \cdot c_P]_{coal} + [m \cdot c_P]_{water}) \cdot \Delta T. \tag{1}$$

Experiments were carried out for different initial water contents of coal and several amounts of added water.

In addition to the wetting experiments, lignite coal samples of fraction B (equidistant cylindrical baskets of 3200 ml) were exposed to a high humid surrounding. At the time where the temperature in the middle of the specimen reached the oven temperature, the oven was flushed with saturated water vapour for 28 minutes. An evaporator outside of the oven was used to produce saturated water vapour, which was piped into the oven on the surface of the coal sample. The mass flow rate of the flushed water vapour was 0,00016 kg/s. Likewise the wetting experiments, the coal samples were stored with an oven temperature below its SIT (here 98°C).

During all experiments, the temperatures of the specimen were measured in the middle of the bulk phase by thermocouples of type K.

EXPERIMENTAL RESULTS

The influence of the oxygen concentration in the surrounding of the specimen on the SIT is shown in Figure 2.

As expected, the SIT of all dusts decreased with a higher volume/surface ratio (V/A). This trend was still present for all experiments with reduced oxygen concentration.
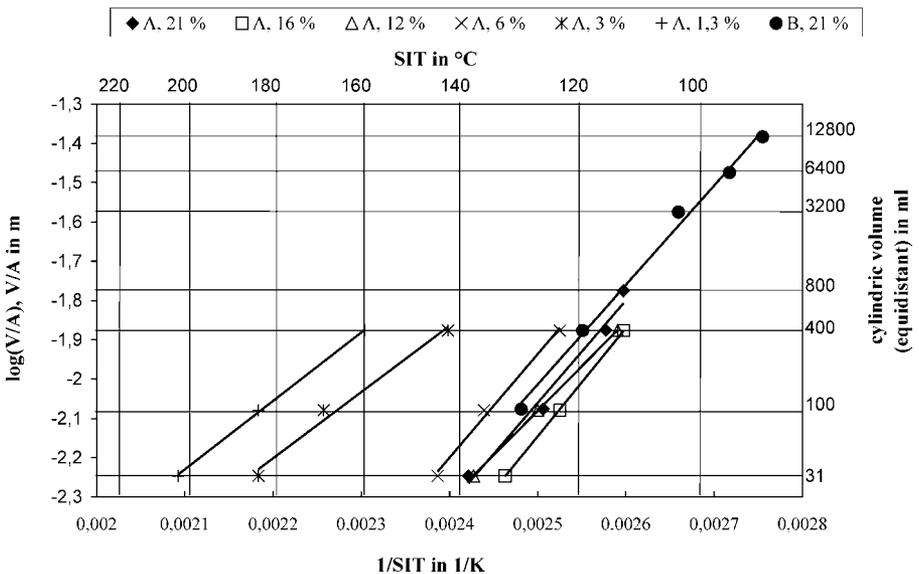

Figure 2. Self-ignition temperatures for German lignite coal in the dependence on the volume-to-surface-ratio (V/A)

Due to the lower availability of oxygen in the surrounding, the SIT of a certain volume dramatically increases with a reduced oxygen concentration. For the investigated materials no oxygen concentration could be found, were self-ignition was prevented. Even for extremely low oxygen concentrations of 1,3 % oxidation reactions of the bulk material could be observed.

In addition, a linear smoothing function for log(V/A) vs. 1/SIT could be found for every investigated oxygen concentration. This behaviour still allows an extrapolation of the SIT to higher V/A-ratios, even for strongly reduced oxygen concentrations.

Note that a reduction of oxygen concentration leads to much slower reactions with lower oxidation temperatures. Due to this change in the reaction mechanism for reduced oxygen concentrations, it was difficult to distinguish between "ignition" and "non-ignition" of the dust sample after the heat storage experiment. This behaviour occurred as soon as the oxygen concentration was reduced down to less than 6%. Consequently, the slope of the linear smoothing function of the strongly reduced oxygen concentrations (3 and 1,3%) is different (smaller) compared to all other concentrations (6, 12, 16, and 21%), see Figure 2.

The influence of wetting on the SIT is shown in Figure 3, where the temperature-time distributions of a 3200 ml sample (lignite coal fraction B) are given for three different oven temperatures. Without adding water on the specimen, the coal ignited with an oven temperature of 104°C. In contrast, with a reduced oven temperature of 103°C another
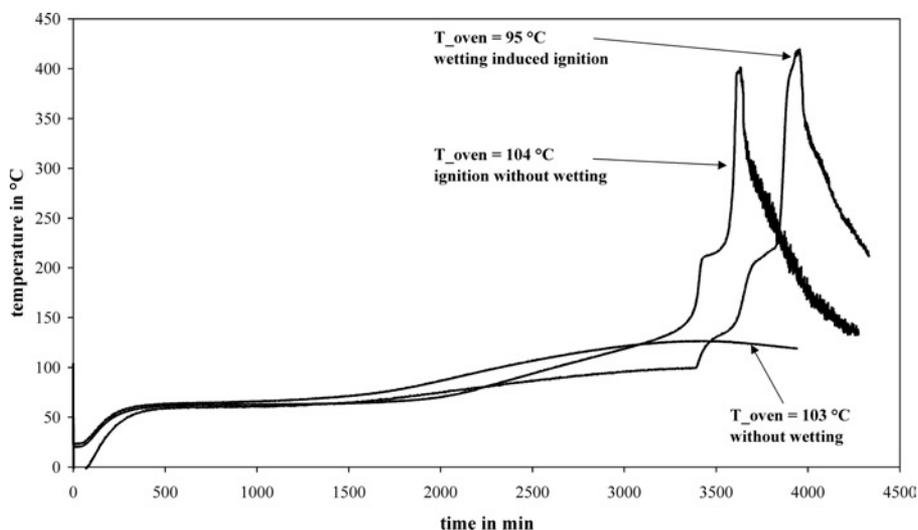

Figure 3. Temperature-time distributions of 3200 ml samples of lignite coal fraction B for different oven temperatures, with and without wetting

specimen of the same size did not ignite. Consequently, all samples of this size stored with an oven temperature of less than 104°C are sub-critical.

After pouring water on the specimen at the time of its maximum temperature, the coal sample became super-critical and ignited even with oven temperatures of 98 and 95°C. This effect was observed until the oven temperatures in other experiments with the same size of the specimen were reduced down to 93°C, when even with wetting no ignition occurred. In consequence, the SIT of 3200 ml lignite coal fraction B was reduced by 10 K down to 93°C due to the effects of wetting.

Experiments with 6400 ml of lignite coal fraction B are presented in Figure 4. The determined SIT of the 6400 ml sample with 21% oxygen content in the surrounding was 95°C.

In this case, wetting of the specimen lead to a reduction of the SIT of 6 K down to 89°C, when no ignition occurred.

The influence of the amount of added water on the heat of wetting for various initial water contents of the coal sample is shown in Figure 5. For a certain initial water content the heat of wetting first increases with the amount of added water, until it reaches a maximum value. Due to less free places for the water molecules to adsorb on the coal particles, the heat of wetting decreases as expected with an increasing initial water content.

In addition to the wetting experiments, the influence of the condensation of saturated water vapour on the SIT is shown in Figure 6. A sub-critical 3200 ml sample of lignite coal fraction B ignited, after water vapour condensed on the surface of the
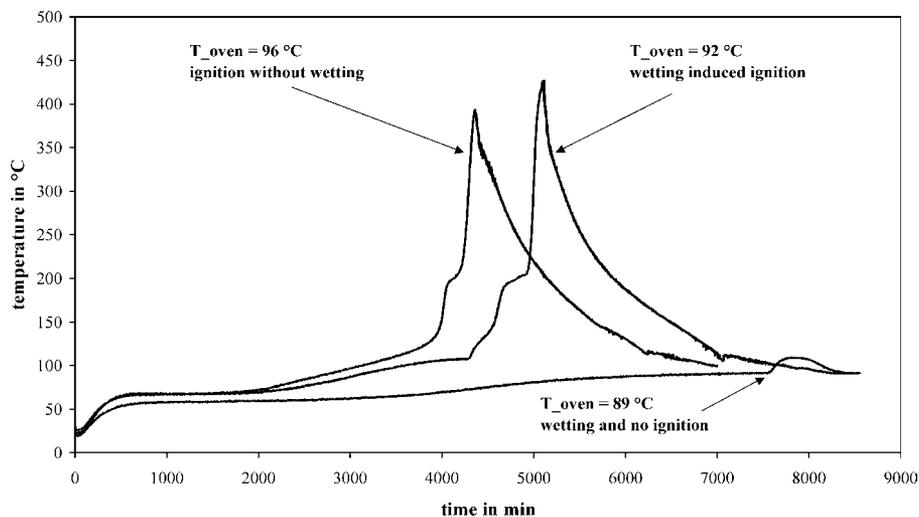

Figure 4. Temperature-time distributions of 6400 ml samples of lignite coal fraction B for different oven temperatures, with and without wetting
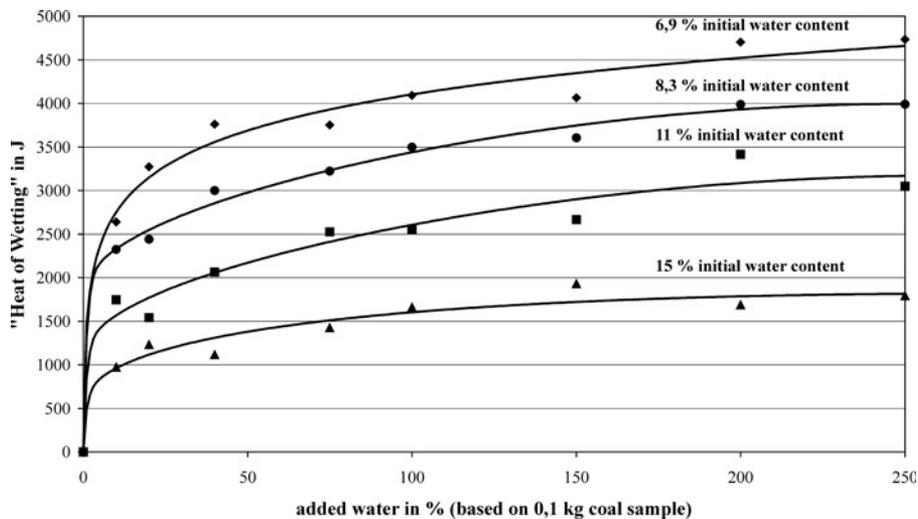
Figure 5. Heat of wetting in the dependence of added water for different initial water contents
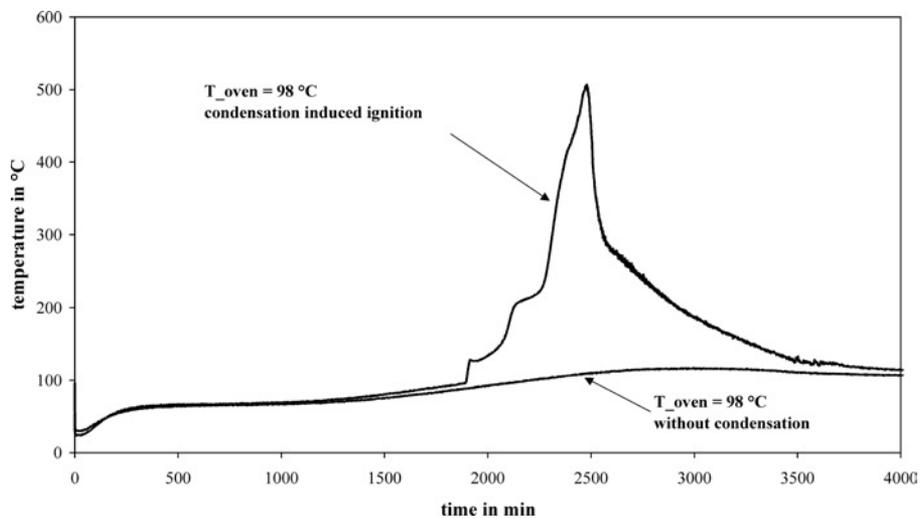

Figure 6. Temperature-time distributions of 3200 ml samples of lignite coal fraction B with an oven temperature of 98°C, with and without condensation for water vapour
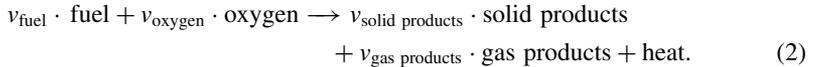
specimen. In consequence, the SIT of this sample was reduced due to the extra heat that was released into the coal sample (condensation of water vapour followed by the heat of wetting).

NUMERIC MODELLING

Numerical simulations are often used to complement extensive experiments and to get prognosis for other geometries and V/A-ratios. In this paper a model is proposed, which covers the effects of self-heating and ignition of combustible bulk materials, evaporation and condensation of water inside the bulk phase. The following assumptions were made:

- only diffusive transport mechanism inside the bulk material (heat and mass transfer)
- material properties as well as diffusion coefficients remain constant
- modelling geometry is homogeneous and isotropic.

The simulations are based on the following simple reaction model eq. (2):

$$v_{\text{fuel}} \cdot \text{fuel} + v_{\text{oxygen}} \cdot \text{oxygen} \longrightarrow v_{\text{solid products}} \cdot \text{solid products}$$
$$+ v_{\text{gas products}} \cdot \text{gas products} + \text{heat.} \qquad (2)$$

The transport mechanisms are described with the following transient equation (3):

$$\frac{\partial \Phi_k}{\partial t} = \Gamma_k \, \text{div}(\text{grad } \Phi_k) + S_{\Phi_k}. \qquad (3)$$

The model consists of eight coupled equations, solving the temperature and concentrations fields of seven species k: fuel, oxygen, solid product (SP), gas product (GP), nitrogen, water and water vapour. The time dependence of the temperature and concentration are described on the left side of eq. (3), the right side represents the transport and source term.

Solving the concentration fields, eq. (3) becomes Fick's 2nd law. For the simulations, fuel was chosen to be the leading species. The source term for fuel is represented with a second order Arrhenius law eq. (4):

$$S_{fuel} = -\left(\frac{C_{fuel}}{C_{fuel,0}}\right)^A \cdot \left(\frac{C_{oxygen}}{C_{oxygen,0} + C_{GP}}\right)^B \cdot \rho_b \cdot k_0 \cdot \exp\left(-\frac{E}{R \cdot T}\right). \qquad (4)$$

The reaction rates of oxygen, solid product and gas product are specified with eq. (5):

$$S_k = \left(\frac{v_k}{v_{fuel}}\right) \cdot \left(\frac{M_k}{M_{fuel}}\right) \cdot S_{fuel}. \qquad (5)$$

The stoichiometric coefficients ν are negative for educts and positive for products, while the reaction rate of nitrogen is zero. The source term of liquid water and vapour is given by eq. (6) and (7):

$$S_w = -EV \cdot C_w \cdot \exp\left(-\frac{E_w}{R \cdot T}\right) + CD \cdot C_v \tag{6}$$

$$S_v = -S_w. \tag{7}$$

The first part of eq. (6) represents the evaporation of the (initial) liquid water and the second part the condensation of the water vapour inside the bulk material. Note that condensation only takes place, if the relative humidity at that point in the bulk phase becomes one.

Concerning the temperature field, eq. (3) becomes the Fourier equation with the following source term eq. (8):

$$S_T = \frac{1}{\rho_b \cdot c_{P_B} + C_W \cdot c_{P_W}}$$
$$\cdot [-S_{fuel} \cdot \Delta H_{fuel} - S_{SP} \cdot \Delta H_{SP} - S_{GP} \cdot \Delta H_{GP} + S_W \cdot \Delta H_V]. \tag{8}$$

The density ρ_b of the bulk material covers the concentrations of all species k.

SIMULATION EXAMPLE

The self-ignition process of a 400 ml equidistant cylinder of lignite coal fraction A was calculated with the model described above. A two-dimensional geometry was applied for this case, to characterize the middle cross-section area of the given sample. The experimental SIT for this V/A-ratio was found to be 115°C.

In Figure 7 the calculated temperature-time distributions of the middle of the specimen for two oven temperatures are illustrated. An ignition occurred with the oven temperature of 120°C, and a reduction down to 119°C leads to a non-ignition of the sample. Thus, the simulated SIT for this cylinder is 119°C and compared to the experimental result an increase of 3,4% (4 K).

CONCLUSIONS

The self-ignition of dusts and solid bulk materials takes a major part in the process safety, and some influences on the SIT are not sufficiently investigated so far. This paper presents the results of the influence of oxygen content in the surrounding, heat of wetting, evaporation and condensation of water in the bulk material on the self-ignition procedure. It has been found, that the SIT for dusts and bulk materials increases with a decreasing oxygen content in the surrounding. Furthermore, for German lignite
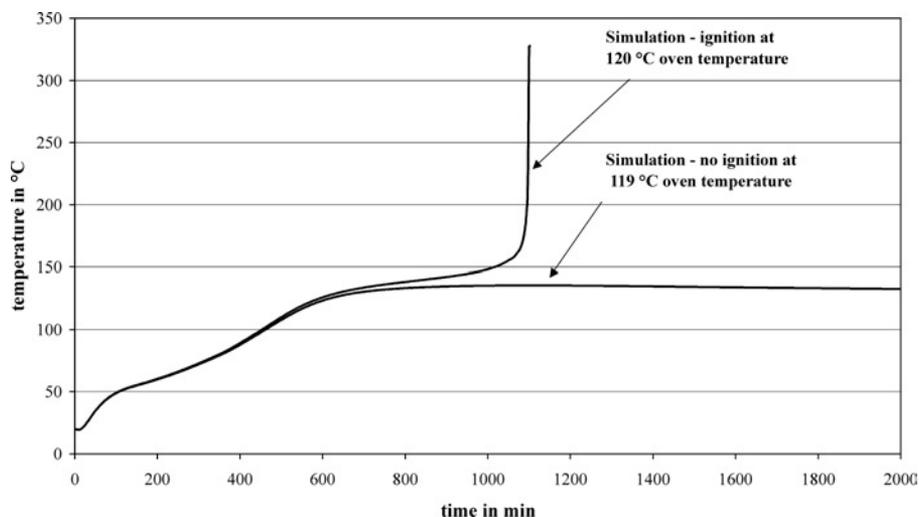
Figure 7. Simulated temperature distributions of a 400 ml cylinder of lignite coal fraction A for two different oven temperatures

coal no oxygen concentration could be found where self-ignition was prevented. Even for strongly reduced oxygen contents of 3 and 1,3% in the surrounding of the specimen oxidation reactions were observed. At these oxygen contents a change in the reaction mechanism took place, leading to much higher oxidation times and lower oxidation temperatures. Consequently, the distinction between ignition and non-ignition after the heat storage experiments became more difficult, because not all of the material was converted.

Besides the oxygen content in the surrounding, water influences the SIT as well. Experiments showed, that wetting can turn a sub-critical into a super-critical deposit of dusts and finally lead to an ignition. Thus, the SIT of a certain volume can be reduced by pouring water on the surface of a bulk material. It has been found, that the SIT for a 3200 and 6400 ml cylindrical basket of crushed lignite coal were reduced by approximately 10 K respectively 6 K due to the wetting of the material. In addition, a sub-critical deposit of crushed lignite coal was turned into a super-critical one, after water vapour condensed on the particles. As well as the wetting itself, the condensation leads to a significant reduction of the SIT for a certain volume.

Additionally, a mathematical model was established, which covers the effects of self-heating, water evaporation as well as condensation. This application allows a prediction of the SIT for different V/A-ratios as well as other geometries. The calculated SIT agreed well with the experimentally determined SIT of the investigated dust sample.

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NOMENCLATURE

A	m^2	surface
C	kg/m^3	concentration
CD	$1/s$	condensation factor
c_P	J/kgK	heat capacity
E	J/mol	activation energy
EV	$1/s$	evaporation factor
k_0	$1/s$	pre-exponential factor
m	kg	mass
M	$kg/kmol$	molecular weight
Q	J	heat of wetting
R	$J/molK$	gas constant
S	kg/m^3s	source term for temperature and concentration fields
t	s	time
T	K	temperature
V	m^3	volume
ΔH	J/kg	calorific value
ΔT	K	temperature difference
Φ	$K; kg/m^3$	temperature resp. concentration parameter
ν	–	stoichiometric coefficient
Γ	m^2/s	transport coefficient (temperature or concentration)
ρ	kg/m^3	density

INDICES

0	initial
A	first coefficient in fuel source term
B	second coefficient in fuel source term
b	bulk material
GP	gas products

k	species
SP	solid products
v	vapour
w	water
T	temperature