Experimental research with the help of thermal derivatographic analysis on coal powder that can be blowed in the furnace

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Abstract. In an integrated steel flow, the costs related to the consumption of metallurgical coke represent approx. 25% of the production cost of the shards obtained by continuous casting. As the price of coal returns to about 50% of that of coke, the technology of insufflating coal dust at the blast furnaces mouths, which transfers the coking process to the blast furnace, can reduce the cost of slag by 4-5%. It cannot be used to blow into the furnace any type of coal. The coal used must meet certain requirements, based on its physical and chemical properties. By thermo-derivatographic analysis, important properties of coals can be established. The authors present in this paper the results of thermal derivatographic analyzes performed on certain types of coal.

1. Introduction

The problem of reducing the specific consumption of coke is topical and according to the opinion of several researchers will continue, as the rate of reduction of coke consumption is and will be lower than the growth rate of cast iron production so that even at a consumption of about 300 kg / ton of cast iron, the coke requirement will be doubled compared to the current one [1], [2], [7] and [8].

Given the economic impact of the most efficient use of coal dust (PC) blast furnace technology, the development of combustion intensification research is currently being observed.

For this purpose, the use of mixtures of different types of coal is extended, especially in terms of volatile material content and the possibility of introducing activating additives is mentioned [1-3].

At some kiln sections, mechanized mixing stations are implemented that allow precise dosing to obtain complex products with high machinability and superior pneumatic and combustion transport properties.

The technique of thermal analysis for research of some characteristics of the combustion process of coal dust and of its intensification methods with application to furnaces is used in different research institutions worldwide, being communicated the results obtained in France and Ukraine [1-5].

Thermal analysis methods aim to investigate the thermal phenomena that arise when a solid is heated or cooled [5],[6].

The methods can be classified according to the purpose pursued, in:
- methods that determine temperature variations;
- methods, by which mass variations are determined.
They can also be classified according to the coordinates in which the thermal curves are recorded:

- methods based on sample temperature recording - also known as temperature curve methods;
- methods by which a certain function of sample temperature is recorded - respectively methods of functional thermal curves.

The method of temperature curves refers to the relationship between sample temperature and time or to sample temperature as a function of ambient temperature (oven).

The group of functional thermal curves mainly refers to the method of recording differential thermal curves and to the differential thermal analysis ATD.

Here are all the variants of thermal analysis that measure and record the difference between the temperature of the sample and the temperature of an inert thermal substance, depending on the time or temperature.

In order to know at any time, the temperature according to the heating program, the installation allows the temperature to be measured in the oven or in the thermal substance or in the sample to be analyzed.

When the temperature is measured in the furnace or in the inert material it varies linearly in the unit of time. In the case of its measurement in the sample, the linearity remains constant in principle only in the temperature intervals where no thermal processes take place.

The method of recording gravimetric thermal curves also known as GT thermal gravimetry refers to the thermal analysis that allows the recording of the mass variation of the sample as a function of temperature $T$ or time $t$ [4], [5], [9-11].

The method of drawing gravimetric thermal curves called GTD-derived thermal gravimetry, respectively, comprises the methods of thermal analysis that record the speed of mass variation, respectively the derived mass variation of the sample as a function of time or temperature.

The thermal conductivity and specific heat of the sample rarely correspond perfectly to those of the aluminum oxide used with the inert substance.

For this reason, the DTA galvanometer can permanently show a temperature difference between the inert material and the sample, which will at the same time lead to the one-way movement of the baseline.

This difference can be mitigated by changing the nature of the inert material and its mass or by diluting the sample with the inert material.

In principle, the methods of thermal analysis can be considered as a function of the temperature of the inert substance or of the furnace in relation to time (linear heating rate).

More recently, with the development of modern derivatography, preference is given to reporting the sample temperature.

- By drawing the DTA curves. TG and DTG are a function of time but can also be considered as functions of temperature as they can be correlated with the temperature of the sample or inert material.
- It is essential for the reproducibility of the DTA, TG and DTG curves that the furnace heating takes place linearly. Under the conditions, of a constant heating speed of the furnace and a linear heating program (normally $10^\circ C / \text{min}$).

The variation of the sample temperature can be controlled.

The DTG curve greatly facilitates the quantitative understanding and appreciation of the basic TG curve.

The reactions that take place in the researched sample that follow one another or that partially overlap on the TG curve, appear on the different DTG curve and can thus be studied separately.

The shunt device based on the electromagnetic induction system detects the slightest change.

2. **Experimental research in the laboratory phase**

The use of derivatographic thermal analysis in the investigation of phenomena related to coal dust combustion is currently accepted internationally.
The details of the method applied differ from case to case. In this first application for ARCELOR MITTAL GALATI they are mainly determined by the characteristics of the analysis installation from the endowment, adopted without major interventions to achieve the proposed objectives.

This aims to:
- assimilation of the working method;
- conducting experiments in rigorous and reproducible conditions;
  - a first evaluation based on the experimental results of the influence of some additives on the PC combustion;
  - obtaining data on the possibility of improving the experimental method.

The equipment being particularly sensitive requires checks and measures to maintain it at an appropriate level of operation.

Some technical issues regarding the recording of the DTG curve could only be remedied during uploads.

The conclusive tracing of the curve is highlighted by maintaining the sensitivity of DTG in the legend of the respective derivatograph.

The conventional thimble shape of the available platinum crucible limits the gasification of the solid organic residue with external oxidizing gaseous agents which preferentially act on the upper part of the layer of material which constitutes the sample.

The parameters of the classical inert material used (alumina calcined at 1200°C) from the fixed crucible, having thermo technical characteristics different (uncompensated) from those of PC, influence the characteristics of the differential thermal curve ATD in absolute terms; In relative terms, however, these records are relevant and comparable.

The tracing of the GT curve conforms to the requirements of the method allowing the quantification of the results of the thermo gravimetric analysis in all experiments.

The plot of the temperature curve (T) is influenced by the material in which it is measured - the inert material or PC (sample).

The temperature of the inert material is close to that of the furnace enclosure and is not influenced by internal thermal effects so that it allows a better linearization of the temperature increase at the indexed speed of ~ 10°C / min in the range 20-1000°C allowed by the installation.

**The equipment used and the way of working**

A MOM derivatograph with photo recording per cylinder was used.

The research material was:
- Coal dust taken from the installation from Blast Furnace Agglomeration Plant from ARCELOR MITTAL GALATI: apron A (representative for current use) and B (special sample with very little ash).

The technical analysis of the samples is presented in Table 1, the granulation is 100% <100 µm with 80% <90 µm.

- The samples from the mixtures were homogenized manually and by grinding.
- After initial tests, samples weighing between 840 and 900 mg were used.

The weighing was done with the semi-automatic balance of the derivatograph (with mechanical operation of the riders).

At each experiment, after loading the film and mounting the cylinder in the installation, the temperature scale was recorded for the max. 1000°C, duration 100 min.

The initialization of the curves was done on the control scale for TG at the level “0”; for T at + 20°C, for DTA at a value of approx. 700°C on a scale of 1000°C and for DTG at the value of approx. 900°C on the same scale.

The heating speed was adjusted to approx. 10°C / min. to fit within 100 min. of the analysis when reaching the final temperature of 1000°C.

In some tests, the heating of the oven was switched off automatically when the temperature exceeded 1000°C.
Table 1. Technical analysis of coal dust samples [1]

| Sample                     | Technical analysis % |
|----------------------------|----------------------|
|                            | W<sup>a</sup> | A<sub>anhy</sub> | V<sub>anhy</sub> | C<sub>anhy</sub> | S<sub>t</sub> |
| PC1- anthracite            | 6.0          | 7.8             | 10.9            | 81.3             | 1.6          |
| PC2- coal with low volatiles | 7.7          | 12.2            | 32.1            | 55.7             | 1.4          |
| PC3- coal with medium volatiles | 6.9          | 11.1            | 33.8            | 55.1             | 0.8          |
| PC4- coal with high volatiles | 6.8          | 10.8            | 35.9            | 53.3             | 0.8          |
| PC5-lignite                | 8.3          | 21.2            | 37.7            | 41.1             | 1.1          |
| PC6- lignite + anthracite mixture | 7.2          | 12.2            | 24.7            | 63.1             | 1.1          |
| PC7- lignite + coal mixture | 8.0          | 16.1            | 36.6            | 47.3             | 2.0          |

The thermal effects recorded when heating the 7 coal samples are presented in the Table 2.

Table 2. DTA thermal effects in °C, over different temperature ranges in °C [1]

| Sample | 140 °C | 300-350 °C | 400-480 °C | 500-585 °C | 625-710 °C | 750-820 °C | 830-940 °C |
|--------|--------|------------|------------|------------|------------|------------|------------|
|        | °C     | °C         | °C         | °C         | °C         | °C         | °C         |
| PC1    | +15    | -21        | +10        | +13        | -11        | +15        | -8         |
| PC2    | +11    | -22        | +13        | -        | -23        | +16        | -6         |
| PC3    | +28    | -22        | +11        | +12        | -8         | +10        | -          |
| PC4    | +34    | -21        | +9         | +14        | -10        | +10        | -          |
| PC5    | +9     | -22        | +10        | -        | -21        | +11        | -7         |
| PC6    | +9     | -23        | +14        | +19        | -14        | +6         | -6         |
| PC7    | +11    | -21        | +19        | -        | -17        | +11        | -5         |

In Figure 1 are shown the DTA curves for all 7 samples to be studied.

Figure 1. Temperature variation of the thermal effects for the 7 coal varieties [1]
For all samples four exothermic thermal effects (identified by increasing the temperature inside the enclosure) were recorded (in temperature ranges 140, 400-480, 500-585 and 750-820°C) and three endothermic thermal effects were determined (in temperature ranges 300-350, 625-710 and 830-940°C).

The variation of the thermal effects indicates the possible development of some internal endothermic processes followed by exothermic processes, manifestation of some phenomena of pyrolysis, oxidation, as well as of the formation of some new compounds.

In the case of both atmospheric regimes an initial portion of the curve is observed which at temperatures of 100-140°C indicates a low loss of mass representing the removal of moisture.

This portion can be followed, but only in the case of oxidizing atmosphere and variable intensity, by a trend mass gain due to chemo-absorption or pre-oxidation (controlled oxidation) and oxygen adsorption phenomena accompanied by low-intensity chemical reactions.

This process of moderate temperature oxidation of solid fuels differs from the "destructive" oxidation that characterizes the proper combustion and leads to the intense formation of CO or CO₂.

Pre-oxidation is characterized by the insertion of oxygen into the macromolecular edifice of carbon without destroying it. Some reaction products such as COOH groups are formed.

The phenomenon is also accompanied by a certain degradation process with the formation of small amounts of CO₂ and H₂O and traces of CO.

The mass of pre-oxidized coal first increases, then decreases, the pre-oxidation being replaced by "destructive" oxidation.

As previously mentioned, such phenomena also accompany the storage of coals in the open air - sometimes causing a enough increase in temperature for self-ignition - a fact also reported in ARCELOR MITTAL GALATI.

This risk increases in inverse relation to the rank of coals being higher in young coals.

The most effective means of preventing self-ignition - in addition to the use of high-grade coals - is the mechanical compaction of the stack layers in order to reduce the free spaces between the pieces of coal by compression in order to prevent air penetration.

The TG curve indicates in the case of argon tests the evolution of volatile material emission without the intervention of external oxidizing gaseous chemical factors.

When heated, solid fuels chemically transform giving rise to volatile products (water, tar, benzene, gas) and form a solid product (coke, semi-coke).

These are pyrolysis reactions. Pyrolysis is the chemical expression of the thermal transformations of solid fuels that form various products in different proportions and which, depending on external oxidizing factors, participate in combustion.

Under certain conditions, this process can cause the appearance of the respective carbon black and the black foam at the Blast Furnace Agglomeration Plant of ARCELOR MITTAL GALATI blast furnaces where coal dust is blown.

During the laboratory experiments the appearance of volatile material was signalled by the evacuation from the furnace of a white smoke with a characteristic smell and visible especially in the tests in inert atmosphere.

The onset temperature of pyrolysis reactions is marked by the appearance of tar. In the case of slow and constant speed heating, it is approx. 350°C for coal.

The tests performed also verify that the pyrolysis process with the release of condensable products ends at 550°C. Non-condensable gas degassing continues (H₂, CH₄, CO₂, CO, N₂, etc.).

3. Results and discussions
Research on the intensification of coal dust combustion carried out with the help of thermal analysis aimed at studying in laboratory conditions some phenomena characteristic of coal dust combustion at tuyeres. of the blast furnace.

Two types of coal were studied comparatively:
- coal with a high content of volatile materials (France coal with 32.2% volatile material);
- coal with a low volatile matter content (RSA semi-anthracite with 10.9% volatile material).

In a first step, the combustion process of the PC was investigated by means of a vertical tubular furnace with a drop type heated to 1500 K.

The particles of coal dust in small quantities (5 mg) were introduced by means of a feeding device on the upper part of the oven tube made of alumina and electrically heated.

After passing through it in free fall, the resulting (residual) semi coke particles were collected in a cooled chamber.

The experiments were performed in a nitrogen atmosphere for the study of pyrolysis and air for the research of pyrolysis and combustion.

In a second stage, the comparative study of the reactivity of the semi coke of the residue was performed in the presence of gases of similar composition to those in the furnace array with approx. 5% CO\(_2\), the experiments being performed with the help of a Mettler thermal balance (derivatograph type thermal analyser).

The flat platinum crucible (≤ 5 mm) with the researched semi-coke sample was kept in direct contact with the welding of the Pt-Pt-Rh thermocouple.

The research methodology provided:

- experiments under heating conditions with a linear increase in temperature (10 K/min) from 25 to 1500 K, in an atmosphere of constant chemical composition (5% CO, 25% CO\(_2\), 70% N\(_2\)), the flow being 60 N l/ min; the evaluation of the results was done by comparing the TG 50 index defined as the temperature which corresponds to a mass loss of 50%;
- experiments at constant temperature (isothermal regime) to determine the reaction constants; the semi-coke sample was initially heated in N\(_2\) to a certain temperature, after which the reactive gas having the above chemical composition is introduced in place of N\(_2\).

The experimental works showed that in the falling furnace heating speeds of 104 - 105 K/s and contact times of 200 - 500 ms were achieved.

This regime ensures the removal of volatile material and a partial to advanced combustion of the solid residue.

Table 3 shows the pyrolysis and combustion tests of coal dust to obtain a semi-coke (combustion residue) like that of tuyeres, where the degree of combustion does not exceed 70-80%.

In order to investigate the gasification conditions of this product outside the proper combustion zone, reactivity determinations were performed according to those shown above in a thermogravimetric analysis installation in the presence of an atmosphere of approx. 5% CO\(_2\) that reproduces the gases in the furnace array.

### Table 3. Results of pyrolysis and combustion experiments of coal dust in N\(_2\) and air Loss of mass of coal dust in vertical furnace with drop, % [1]

| Particles size, μm | 100-125 | 200 – 250 |
|-------------------|---------|-----------|
|                   | 1000    | 1200      | 1400      | 1000    | 1200      | 1400      |
| Coal with 32,3% volatile material in N\(_2\), % | 50.7 | 54.9 | 56.1 | 44.9 | 47.1 | 53.0 |
| Coal with 32,3% volatile material in air, % | 65.9\(^{l}\) | 68.6\(^{l}\) | 73.7\(^{l}\) | 77.2 | 88.7 | 91.2 |
| Coal with 10,9% volatile material in N\(_2\), % | 8.8 | 10.1 | 10.8 | 8.2 | 9.2 | 10.3 |
| Coal with 10,9% volatile material in air, % | 57.8 | 82.3 | 88.4 | 28.5 | 57.6 | 68.9 |
The structure of the two coal varieties shows marked differences after the treatment of pyrolysis in N2 and pyrolysis and combustion in air, respectively.

In the case of high-volatile coal (coal), the semi-coke particles take on an empty spherical shape inside, indicating that during the process the coal has passed through a plastic phase.

In contrast, residual coal particles with few volatiles (semi-anthracite from RSA) retain their original angular shape with sharp edges without the indication of the appearance of a plastic phase. Numerous cracks and pores are also observed.

Spherical surface determinations were also performed by adsorption with N2 and CO2 (BET).

The reactivities were determined with the Mettler thermogravimetric analyzer in the two mentioned heating variants (linear and isothermal).

The device is specially designed for determinations in different atmospheres or vacuum. This quantity was chosen as a reactivity comparison parameter. The results are presented in Table 4.

| Coal with 32.2% volatile material | Primary treatment | Reactivity |
|-----------------------------------|-------------------|------------|
| Coal with 32.2% volatile material | 200-250 μm        | 1000 N2    | 1195 |
|                                   |                   | 1200 N2    | 1235 |
|                                   |                   | 1200 N2    | 1170 |
| Semiantracit with 10.9% volatile material | 200-250 μm | 1000 N2    | 1330 |
|                                   |                   | 1200 N2    | 1305 |
|                                   |                   | 1200 N2    | 1250 |
| Semiantracit with 10.9% volatile material | 100-125 μm | 1000 N2    | 1310 |
|                                   |                   | 1200 N2    | 1295 |
|                                   |                   | 1200 N2    | 1295 |
|                                   |                   | 1400 N2    | 1280 |

The TG 50 values are between 1135 and 1235°C for the coal residue (semi-coke) with a high volatile material content and between 1170-1330°C for the low volatile material.

The higher reactivity of the first batch is observed, signalled by the lower values of TG 50. For comparison, determinations were made with a fine coke of the same granulation (100 -150 μm) finding TG 50 = 1410°C, in the same conditions.

The degassing rate as a function of temperature is shown for coals with different volatile material contents and different degrees of carbonization.

The curves show that the temperature of the beginning of the decomposition of the coals varies depending on the degree of carbonization and the volatile material content between 320 and 440°C. The rate at which pyrolysis products are released also varies. It is observed that the temperature at which the release rate is maximum is between 400 and 550°C.

A high volatile material content of the coal dust favors the initiation of the combustion process, leads to a higher degree of combustion and less residues (semi coke).

Disadvantages include: the tendency of coals in this category to self-ignite during storage and use and the tendency to form carbon black and black foam when blown into the furnace.

The volatile material concentration is conventionally determined according to STAS 5268 for the temperature of 850°C, an internationally accepted value, close to that of the regime in coking batteries.

Under blast furnace conditions, however, degassing processes take place at significantly higher temperatures.
In order to know the influence of temperature on volatile material emission, laboratory experiments were initiated which aimed to correlate the amount of volatile material resulting with the temperature of the pyrolysis process, maintaining the heating time unchanged according to STAS.

At a later stage, the influence of the heating rate on the volatile material emission is also of interest. The applied method consists in heating in the absence of air for 7 min. at temperatures of 850; 1000; 1100 and 1200°C of coal dust samples with a particle size of 80% <0.09 mm.

The mass loss of the analyzed fuel is equal to the sum of moisture and volatiles. The volatile matter content results from the difference between the total loss of mass and that caused by moisture determined separately.

The equipment used consists of a horizontal oven with a plug that ensures a heating temperature up to 1500°C, with resistors and thermostat to maintain the indexed temperature;
- thermocouple Pt – Pt-Rh;
- quartz crucibles provided with lids.

Table 5 presents the technical analysis of the researched samples from imported coal for ARCELOR MITTAL GALATI. Sort A is a coal dust taken from the grinder and Sort B is a special selection poor in ash.

| Type of coal | W<sub>a</sub> | A<sub>anh</sub> | V<sub>anh</sub> | S<sub>anh</sub> | C<sub>fix</sub> |
|--------------|--------------|----------------|----------------|----------------|-------------|
| A            | 1.74         | 8.21           | 35.6           | 0.89           | 55.3        |
| B            | 3.56         | 2.57           | 39.41          | 0.63           | 57.39       |

In Table 6 are presented the experimental conditions.

| Temp. °C | Heating speed °C/min | Coal A | Coal B | Average |
|----------|----------------------|--------|--------|---------|
|          |                      | A1     | A2     | average | B1      | B2      | Average |
| 850      | 121                  | 35.74  | 35.48  | 35.61   | 39.67   | 39.41   | 39.54   |
| 1000     | 143                  | 37.67  | 37.60  | 37.64   | 40.29   | 40.26   | 40.28   |
| 1100     | 157                  | 38.42  | 38.33  | 38.38   | 41.07   | 41.36   | 41.22   |
| 1200     | 171                  | 39.08  | 38.92  | 39.00   | 42.18   | 41.80   | 41.99   |

The results confirm the increasing trend of volatile material emissions with the temperature and heating rate influenced by the coal apron. At 1200°C the emission reaches 39% for coal type A, increasing by about 9.5% (rel.) Compared to that of the temperature of 850°C, while for coal B richer in volatile material the increase is 6.2% (rel.) for 42% volatile material.

The increasing trend of volatile material emission with temperature and especially with heating speed is also verified by the experiments of other profile laboratories abroad that indicate values up to 1.7 times higher at heating rates of 104-105°C/s.

4. Conclusions

The coke has significantly lower reactivity characteristics than the coal dust residue at the exit from the combustion zone.

Following the constant speed heating of the coals, the organic substance decomposes, forming compounds with a lower molecular weight, in a gaseous state, which tend to leave the organic mass.

The volatile matter content in relation to the coal mass of the coal represents a basic characteristic both from the point of view of the coal classification and the determination of the geological age of the deposit and of the combustion properties.

This confirms the possibility of preferential gasification of residual PC in the furnace outside the combustion zone in front of the tuyeres.
The results are an experimental support that indicates the possibility of advanced recovery of PC in the furnace, even if the combustion at tuyeres cannot be practically complete due to the very short time and specific conditions.

For the full recovery of the coal dust injection in the blast furnace, in addition to the gasification reaction investigated, the participation in direct reduction processes, cast iron carburization, etc. can be considered.

Thus, there are the premises of an advanced gasification with the formation of small amounts of solid residue but also of the possibility of the formation of carbon black in the absence of an enough supply of oxidizing substances and an efficient contact mechanism.

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