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LOW-TEMPERATURE OXIDATION OF COAL

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ABSTRACT

An overview is given of the possibilities thermal analysis and in particular thermogravimetry has in studying low-temperature oxidation of coal. First, procedures are described with which representative samples of coal can be obtained. Secondly, the oxygen consumption of coal has been measured using a sensitive vacuum microbalance, coupled to a mass spectrometer to analyze the effluent gas. Finally, with infrared spectroscopy structural changes at the coal surface, due to low-temperature oxidation are determined.

INTRODUCTION

When coal is heated in an oxygen atmosphere at temperatures above 300 °C combustion processes set in. A DSC curve of this process reveals two exothermic peaks. The first is associated with the formation of quinone-like structures at the surface of the coal, the second with the combustion of the total coal skeleton (1).

The formation of those quinone-like structures proceeds with the uptake of up to several per cent of oxygen. As this exothermic oxygen consumption also proceeds at lower temperatures, it leads to spontaneous heating or even self-ignition of the coal. Due to low-temperature oxidation, the processing characteristics of coal may decrease considerably. In particular, this holds for the calorific value, which may change by several per cent.

Consequently, detailed studies were carried out to predict or to prevent spontaneous heating and to study the corresponding chemical changes in coal (2-6).

This paper describes the possibilities thermal analysis, and in particular thermogravimetry offers in studying the low-temperature oxidation of coal.

THE STRUCTURE OF COAL

The term 'coal' is applied to a wide range of materials, from brown coals to anthracites. Coals throughout this range differ from each other in appearance, analysis and structure. Therefore one specific chemical structure of coal does not exist.

It is however possible, within a certain rank, to define general structural features of coal. The fundamental skeletal structure of a bituminous vitrinite consists of clusters of condensed aromatic nuclei. For coals containing up to

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90 % carbon these clusters contain on average three rings, but the cluster size increases very rapidly when the carbon content increases. The aromatic clusters are connected to each other by means of aliphatic carbon structures and also by oxygen, nitrogen and sulphur links (1). A proposed model of a 'molecule' of a bituminous vitrinite is given in fig. 1; the above-mentioned structural features are clearly reflected*.

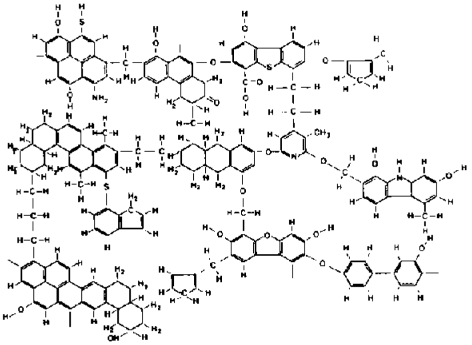

Fig. 1. A model of a bituminous vitrinite.

SAMPLING OF COAL

Structural investigations of coal are considerably hindered by the very heterogenic nature of coal.

This heterogenic nature can easily be understood if it is taken into account that coal in fact is a product of a reaction which is not completed yet. The structure, consequently, depends on two factors: the nature of the reacting components and the reaction parameters (time, temperature, pressure). It is clear therefore that the coal structure may vary extremely, even in the case of coal which originates from one and the same seam.

When carrying out investigations on coal, ample precautions must be taken to ensure that the analyses are carried out on representative samples. Unfortunately, a great deal of published results are lacking on this point, which means that results cannot be inter-related etc. To ensure the representativity of coal samples, the Dutch Centre for Coal Specimens, SBN**, was founded. This centre collects coal samples from different countries and locations in amounts of about 1000 kg.

These samples are ground in a nitrogen atmosphere to pass a sieve of 10 mm and by means of a spinning riffler divided into 10 fractions of 100 kg.

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*We would like to emphasize here that figure 1 is just an illustration of a possible coal molecule. A large number of those molecule models are proposed in the literature, each with its intrensic merits and demerits.

** SBN, P.O.Box 151, 6470 ED, Eygelshoven, The Netherlands

Nine fractions are stored in hermetically sealed containers at a constant temperature of 10 °C.

One sample is ground again to pass a sieve of 3 mm and divided into fractions of 10 kg. From these fractions laboratory samples are prepared, which can be supplied to every laboratory carrying out investigations on coal.

EXPERIMENTS

The low-temperature oxidation study has been carried out using a 1 kg sample of coal obtained from SBN, coded 7 DE, and originating from the Aachener coal basin (Emil Mayrisch seam I_0).

The sample was divided into fractions of 100 g. (by means of a spinning riffler). A 100 gram sample was ground to pass a sieve of 100 µm and divided into fractions of 10 g. From these fractions the samples for investigation were obtained.

DSC measurements were performed using a Perkin-Elmer DSC-2, and TG experiments were carried out with a Perkin-Elmer TGS-2 thermobalance, coupled to a Riber QS 100 B quadrupole mass spectrometer.

Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrometer.

RESULTS AND DISCUSSION

The DSC curve of coal 7 DE, measured in an oxygen atmosphere, is shown in fig. 2. The two exothermic peaks, the first having its maximum at c. 350 °C the second at c. 500 °C, can be clearly distinguished. As stated before the first peak is associated with partial oxidation processes at the coal surface, the second peak with the complete oxidation of the coal.

In figure 2 also the TG curve is given. The weight increase of the sample, due to oxygen consumption is about 6 % up to 350 °C. At higher temperatures naturally, a fast weight decrease takes place.

As the oxygen consumption is responsible for the self-heating of coal,

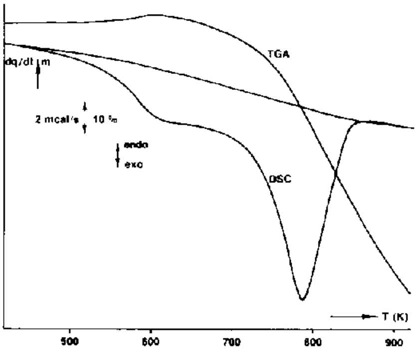

Fig. 2. DSC/TG curve of coal 7 DE.

knowledge on the rate of this oxygen uptake gives insight into the self-heating tendency of the coal. The oxygen uptake can be measured accurately with a sensitive thermobalance. In fig. 3 the measured curves are given, at temperatures varying between 70 and 160 °C.

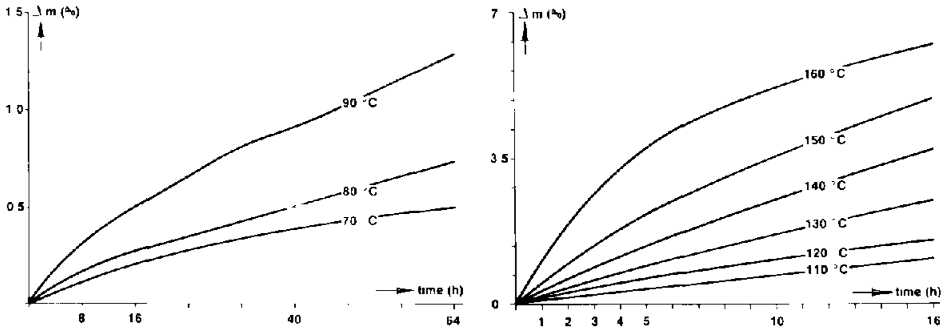

Fig. 3a,b. Weight increase of coal 7 DE at several temperatures.

At a temperature of 160 °C the sample shows a weight gain of 6 % in 16 hours. At 70 °C this weight gain is only 0.5 % in 64 hours. Due to instrumental factors the curves in fig. 3a show some irregularities, which may easily be understood if one realises that the weight gain at 70 °C is only 1 μg/hour. A plot of the derivative of the weight gain curve versus the inverse absolute temperature is shown in figure 4. This Arrhenius-like plot gives a rather straight line, indicating that one rate-determining process is responsible for the weight increase, in good agreement with ref. 1

By means of TG only changes in weight are measured, which need not necessarily be the result of oxygen consumption alone. By means of TG/MS therefore the

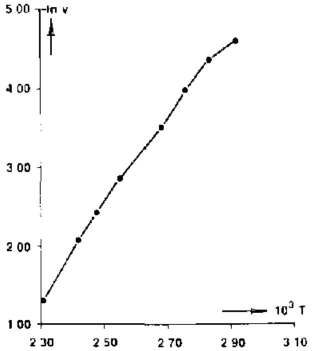

Fig. 4. Rate of weight increase vs. 1/T.

effluent gas was analyzed.

The result is given in figure 5. It can be seen, that at rather low temperatures (< 200 °C) the coal not only consumes oxygen, but also emits carbondioxide and water. This indicates that at the surface of the coal rather complex processes occur. A predominant role must be attributed to the fact that coal is still a very reactive substance, which is reflected by e.s.r.-measurements, which show a large number of free spins (2).

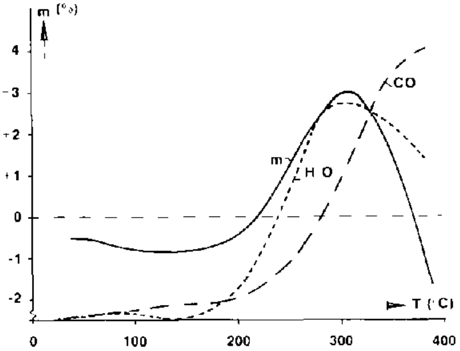

Fig. 5. TG/MS curve of coal 7 DE

In literature several mechanisms for the low-temperature oxidation of coal are proposed (6).

We prefer the following mechanism:

- Initiation $R. + O_2 \rightarrow ROO.$
- Propagation $ROO. + RH \rightarrow ROOH + R.$
  $RH + .OH \rightarrow R. + H_2O$
- Radical displacement
  $ROOH + R. \rightarrow R\text{-}O\text{-}R + .OH$

The initiation step is due to the presence of free spins in the coal. According to Retcofsky (7) the initiation step is, at least partly, reversible.

At somewhat higher temperatures (50-60 °C) the hydroperoxides may degrade:

$$ROOH \rightarrow RO. + .OH$$

eventually giving rise to ether-and quinone-like structures at the coal surface.

The weight increase of the coal is also a result of oxygen consumption on the one hand and evolution of carbondioxyde and water on the other hand. Especially at lower temperatures (< 100 °C) the oxygen consumption is much larger than the carbondioxyde and water emission. This means that with thermogravimetry the rate of oxygen consumption can be measured rather accurately.

Structural changes of a coal as a result of low-temperature oxidation can conveniently be detected by means of infrared spectroscopy. To show that, a sample of coal was oxidized at 130 °C during 24 h. after which it had consumed about 4 % of oxygen. The infrared spectra before and after oxidation are presented in figure 6.

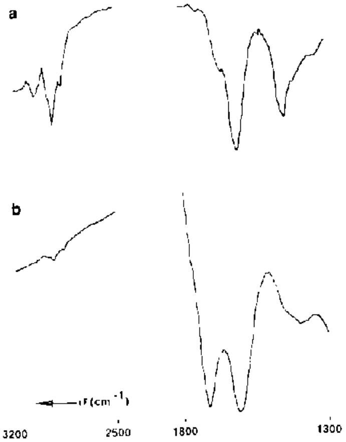

Fig. 6a,b. IR spectra of coal 7 DE
a: as received   b: oxidized during 24 h. at 130 °C

The differences between the curves a and b are very distinct. In the carbonyl stretching region a big absorption band at 1720 cm^{-1} has appeared (ketone) and in the C-H stretching region the absorptions of the aliphatic C-H bonds have almost completely disappeared. This indicates that the oxygen attack starts at the aliphatic places of the coal molecule.

CONCLUSIONS

Thermal analysis and in particular thermogravimetry in combination with a mass spectrometer, is a powerful means in studying the low-temperature oxidation of coal. Oxidation rates can adequately be measured and with a TG/MS combination information on the oxidation mechanism can be obtained.

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