Thermochimica Acta, 114 (1987) 171–178
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

AN APPROACH WITH USE OF EGA TO THE MECHANISM OF SULFUR RELEASE DURING COAL COMBUSTION

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SUMMARY

Coal contains organic, sulfate ($CaSO_4$) and pyritic (FeS_2) sulfur, that are released mainly as sulfur dioxide at different temperatures during coal combustion. The mechanism and rate of sulfur release are studied using TG and EGA (mass spectrometry). The influence of FeS_2 is determined by addition of pyrite to the coal sample.

INTRODUCTION

At the Delft University of Technology research is carried out on the fluidized bed combustion of coal (FBC). The release of sulfur during FBC has to be properly understood in order to choose the right operating conditions for an efficient in-situ sulfur capture. Hereto an approach is made to the sulfur release mechanism with use of TG and EGA. However, the following remarks have to be taken into account.

Thermal analytical techniques are very useful for a detailed study of chemical and physical phenomena in gas/solid reactions. But the use of the results in other processes or other types of equipment is limited when the nature of the phenomena taking place is predominantly dependent on physical/technical limitations of the thermobalance.

This may hold especially for the study of sulfur release with TG and EGA for the use in FBC, while the rate of heating, the supply of oxygen and the mixing of reactants in a Fluid Bed Coal Combustor differ significantly from those in a thermobalance.

Therefore thermal analytical results that give basic insight in coal combustion have to be used with care in scaling-up to FBC conditions.

0040-6031/87/$03.50

EXPERIMENTAL METHODS

TG and EGA experiments are carried out with coal and pyrite in a self-built thermobalance, equipped with a C.I. Electronics microbalance and connected to a Topatron mass spectrometer from Leybold Hereaus. The heating rate is $10^{o}C$/min with a flow rate (air or oxygen) of 100 ml_n/min; samples of 90 to 180 mg are heated to $900^{o}C$.

The relative amount of sulfur dioxide is measured by determining the magnitude of the mass spectrometer signal at mass 64. The mass spectrometer signal is calibrated by using a known sample of pyrite and comparison of the sulfur release peaks.

The analysis data of the coal types are given in Table 1. In the experiments impure pyrite is used containing 67.5 wt% FeS_2, 5.6 wt% FeS and 26.9 wt% inert material.

Also an experiment is carried out with $CaSO_4$.1/2aq and silica in 20 ml_n air/min and heating rate $10^{o}C$/min. The temperature is raised to $1040^{o}C$ where the sample is kept isothermal for 16 minutes.

TABLE 1

Analysis data of coal types (wt%, dry and ash free).

Coal type	volatile matter (%)	ash (%)	organic sulfur (%)	pyritic sulfur (%)	sulfate sulfur (%)
501GB28*)	33.87	24.94	0.96	0.95	1.16
PSOC667**)	44.26	18.73	7.50	7.63	2.15
513DE38*)	41.15	8.14	0.63	0.45	0.01

*) Dutch Centre for Coal Specimens SBN

**) Pennsylvania State Coal Data Base

ORGANIC SULFUR

Organic sulfur is present in coal in many different sulfur containing functional groups (ref.1). Only divalent sulfur is present in coal; the most important compounds are thiophenes, aryl-, cyclic-, alifatic sulfides and aryl- and alifatic thiols. It is assumed here that the S-release from organic sulfur is dependant on the rate of carbon combustion for which strong evidence is supplied by Warne et al. (ref.2).

SULFATE SULFUR

The sulfate sulfur ($CaSO_4$) in coal can react with the coal ash (predominantly SiO_2 (~60 wt%), Fe_2O_3 (~20 wt%) and Al_2O_3 (~15 wt%) to form silicates and SO_2. These reactions have a high temperature dependency (ref.3). Major reaction product reported by Yang et al. (ref.3) after 40% decomposition of $CaSO_4$ at 870°C is $Ca_6Si_3O_{12}$.

In Fig.1 the rate of conversion is given of a reactant mixture of 1 $CaSO_4.1/2aq$:1 SiO_2 (weight). The reaction starts at 980°C and increases fast up to 1040°C at which the sample is kept isothermal for 16 minutes during which the reaction rate decreases. Sulfur dioxide is formed with a maximum release at 1040°C.

So the reaction between $CaSO_4$ and SiO_2 starts 110°C above the temperature at which Yang et al. (ref.3) carried out their experiments with coal ash.

PYRITIC SULFUR

FeS_2 in coal occurs predominantly as microscopic grains or aggregates of micron-size crystals intimately combined with the coal.

The behaviour of pyrite during combustion is considered by several authors (refs. 4-6). It is concluded that the decomposition of pyrite is a complicated process composed of several overlapping reactions.

A general reaction mechanism of pyrite in coal is suggested in Fig.2 based on the literature reported. Reactions (1) and (2) can occur between 330 and 380°C (ref.4):

$$(1-y)FeS_2 + (1-2y)O_2 \rightarrow Fe_{1-y}S + (1-2y)SO_2 \qquad (1)$$

$$2Fe_{1-y}S + (3-y)O_2 \rightarrow 2(1-y)FeO + 2SO_2 \qquad (2)$$

The FeO formed is relatively unstable and oxidizes to Fe_3O_4 above 390°C via reaction (3):

$$3FeO + 1/2O_2 \rightarrow Fe_3O_4 \qquad (3)$$

However, if the oxygen concentration is high and the temperature is further increased reaction (3) will not be observed and hematite is formed (ref.4) via reaction (4):

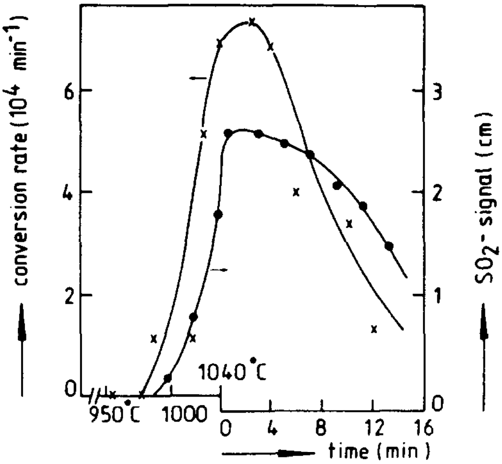


Fig. 1. The conversion rate and sulfur release during the reaction between 84.37 mg $CaSO_4 \cdot 1/2aq$ and 84.37 mg SiO_2 in 20 ml_n air/min and 10°C/min.

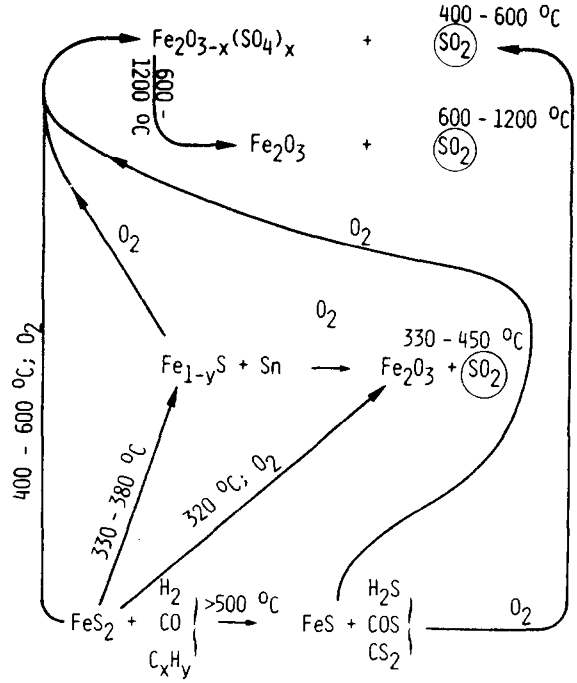


Fig. 2. The reaction mechanism of pyrite in coal.

$2Fe_3O_4 + 1/2O_2 \rightarrow 3Fe_2O_3$ (4)

Iron sulfate can be formed at temperatures between 320 and 450°C (reaction (5)), while further direct oxidation of pyrite is possible (reaction (6)), (ref.5):

$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2$ (5)

$2FeS_2 + 1/2O_2 \rightarrow Fe_2O_3 + 4SO_2$ (6)

Paulik et al. (ref.6) suggest the overall reaction (7) between 400 and 600°C:

$2FeS_2 + (5.5 + 0.5x)O_2 \rightarrow Fe_2O_{3-x}(SO_4)_x + (4-x)SO_2$ (7)

The intermediate will decompose between 600 and 1200°C via reaction (8):

$Fe_2O_{3-x}(SO_4)_x \rightarrow Fe_2O_3 + xSO_2 + \frac{x}{2}O_2$ (8)

Pyrite can also react at temperatures higher than 500°C with products of coal devolatilization as H_2, CO and in general C_xH_y to compounds as H_2S, COS and CS_2 (ref.1), e.g. via reaction (9):

$FeS_2 + H_2 \rightarrow FeS + H_2S$ (9)

So a general reaction mechanism results (Fig.2) showing pyritic sulfur peaks between 330-450°C, 400-600°C and 600-1200°C. The reaction scheme will now be verified by experiment.

According to reactions (6) and (8) the solid reaction product is Fe_2O_3. Combustion of the impure pyrite (78.5 mg FeS_2, 6.5 mg FeS and 31.3 mg inert material) should therefore give a final weight of 120.8 mg, which is in good agreement with the measured 119.3 mg. Sulfur is released from 435°C with a peak between 550 and 580°C, while a further sulfur increase is observed from 625°C to the end of the reaction at 840°C. These oberservations are in good agreement with reactions (7) and (8) of the reaction scheme, Fig.2.

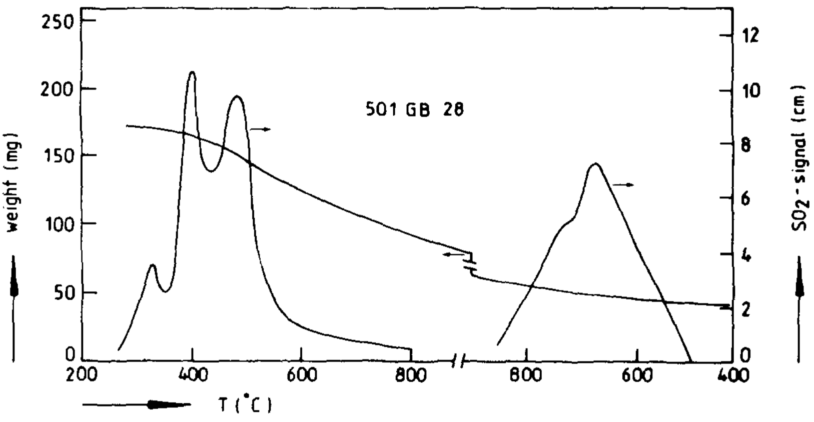
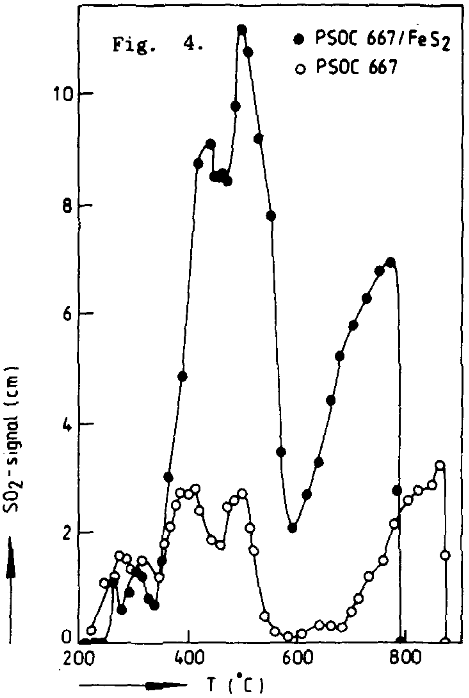


Fig. 3. The weight and sulfur release during combustion of 179.95 mg of coal 501GB28 in 100 ml_n air/min and $10^oC/min$.



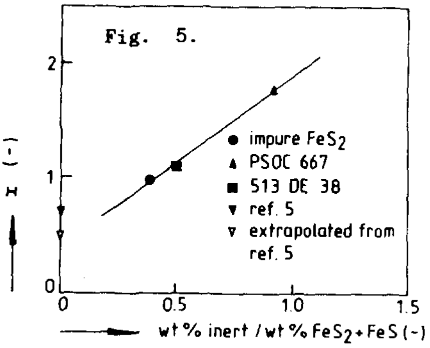


Fig. 4. The sulfur release during combustion of 110.40 mg of coal PSOC667 and of 98.03 mg PSOC667 + 32.46 mg impure pyrite in 100 ml_n air/min and $10^oC/min$.

Fig. 5. The distribution parameter x in $Fe_2O_{3-x}(SO_4)_x$ as function of the ratio between the wt% inert material and the wt% FeS_2 + FeS in the sample.

The sulfur release profile of coal 501GB28 is given in Fig.3 showing four sulfur peaks. The first peak between ~250 and 350°C is attributed to (organic) volatile sulfur. The following peaks are observed between 350 and 430°C (reactions (1-6)) and between 430 and ~650°C (reaction (7)). Then the sulfur release decreases significantly up to 900°C. From this temperature on the coal sample is subsequently cooled in the air flow and a fourth peak is observed between 900 and 500°C, possibly according to reaction (8). The peak disappeared at the moment that the coal is burned out. The appearance of the peaks is in agreement with the reaction scheme presented.

Addition of extra pyrite to coal does not change the position of the peaks but only their height. A typical example of coal PSOC 667 is given in Fig.4. The first small peak between ~200 and 340°C is attributed to volatile sulfur. The increase of the second peak is in accordance with reactions (1-6). The increase of the third peak between 455 and 585°C is in agreement with reaction (7), while the fourth peak between 585 and ~900°C will be caused by reaction (8). Addition of pyrite to coal 513DE38 shows a similar behaviour.

The distribution parameter x in the intermediate product $Fe_2O_{3-x}(SO_4)_x$ is calculated based on the reaction scheme in Fig.2 and by comparison of the magnitude and change of the sulfur peak areas. The parameter x is also calculated from data of Banerjee et al. (ref.5) of the product distribution at different temperatures in the oxidation of synthetic pyrite.

The parameter x is plotted in Fig.5 as function of the ratio between the weight of inert material and the weight of FeS_2 and FeS in the sample. x increases when more inert material is present. This is in agreement with observations of Banerjee et al. (ref.5), who report that the formation of ferric sulfate is strongly increased in presence of silica. Further they conclude that the sulfation of pyrite between 400 and 630°C is the predominant reaction in presence of silica, which catalytic effect may be due to increased adsorption of oxygen on the surface of silica as the rate controlling step.

It is observed in Fig.6 that dependent on the coal combustion rate also only one sulfur peak can remain, starting at the coal ignition at 260°C. In this situation the coal combustion rate is almost 5 times as high as compared to the situation in Fig.3, due to the increased oxygen concentration (coal burnout time of the 180 mg 501GB28 sample is reduced from almost 120 min. to 25 min.). This means that the appearence of

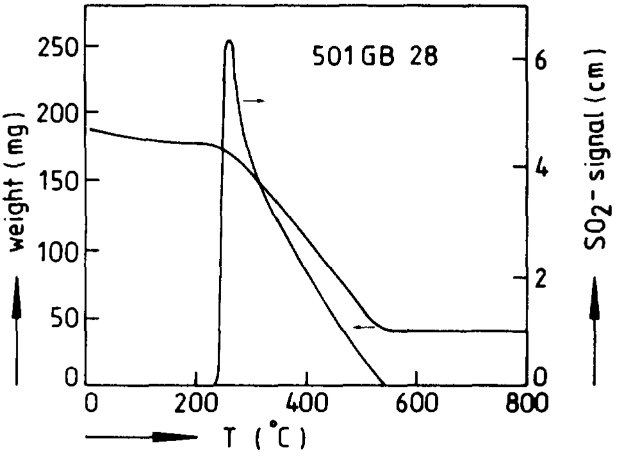


Fig. 6. The weight and sulfur release during combustion of 179.85 mg of coal 501GB28 in 100 ml_n oxygen/min and 10^0C/min.

different peaks in the sulfur release profile of a coal sample during FBC is doubtful, while the average combustion rate is then much higher (burnout time in general 1-2 min.).

ACKNOWLEDGEMENT

The authors wish to acknowledge the cooperation and financial support of the Netherlands Research Foundation STW.

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