

EMISSION OF SULPHUR DIOXIDE DURING THERMAL TREATMENT OF FOSSIL FUELS

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Abstract

The dynamics of SO₂ emission during thermooxidation of Estonian oil shale, its semicoke, different samples of coal and their mixtures, as well as the influence of Estonian oil shale ash addition (for modelling the CFBC process) on the dynamics were studied. The experiments were carried out with thermogravimetric equipment under dynamic heating conditions (5 K min⁻¹) in the atmosphere of dried air, with simultaneous gasitrimetric EGA.

It was established that SO₂ emission from the fuels started at 200–320°C. Depending on the form of sulphur (organic, pyritic, sulphate), the emission took place in two or three steps, and continued up to 580–650°C, during which 35–75% of the total sulphur was emitted into the gaseous phase. Regulating the mole ratio of free CaO/S in the mixtures of fuels with oil shale ash addition the emission of SO₂ ceased abruptly at 460–540°C and it was limited to the level of 7–30%.

Keywords: air pollution, coal, oil shale, semicoke, SO₂

Introduction

Combustion of fossil fuels at thermal power plants cause contamination of the atmosphere with sulphur dioxide. To reduce SO₂ emission into the atmosphere by dry methods, injection of limestone or other alkali compounds into the burner or the gas tract is used.

Energy production in the Republic of Estonia is mainly based on burning of low quality local solid fossil fuel – Estonian oil shale (EOS). EOS is characterised by a low gross heat of combustion value (10.2 MJ kg⁻¹) and a high content of mineral matter (~70%), nearly 50% of which are carbonates (calcite, dolomite), and sulphur (~1.5). The carbonates decompose during thermal treatment of oil shale, with formation of free Ca, Mg-oxides which are the main binders of SO₂ during combustion of fuels. Thus, using the mineral part of EOS or its semicoke, it might be possible to bind the SO₂ formed at co-combustion of EOS with sulphur-rich coals. It should be noted that the solid waste of thermal processing of EOS semicoke is a dangerous source of contamination of soil, water bodies and ground water with phenols, sulphides and other toxic compounds accompanying its storing in dumps [1]. The transformation of sulphur compounds at high-temperature combustion of oil shale (at the flame temperature 1200–1400°C) has been generalized by Ots [2]. The results of investigations of thermal destruction of different oil shales in neutral and oxidational gaseous areas were reported in [3–7]. In fact, these investigations do not deal with

the dynamics of SO₂ emission during thermooxidation of EOS and other solid fossil fuels at temperatures up to 800–1000°C, particularly important when the fluidized bed combustion technology is used.

The aim of the present work was to study the dynamics of SO₂ emission during thermal treatment of different sample of coal, EOS, its semicoke and their mixtures, as well as the influence of EOS ash addition on the dynamics of SO₂ emission.

Experimental

Materials

Four samples of different coals, one sample of EOS, its semicoke and their mixtures with mass ratio 1:1 were investigated. Different forms of sulphur (total, sulphate, pyritic) were determined in the fuels [8]. The content of organic sulphur was calculated as

$$S_{\text{organic}} = S_{\text{total}} - S_{\text{pyritic}} - S_{\text{sulphate}}$$

and the content of organic matter in dry samples as

$$[100 - A^{\text{d}} - (CO_2)_{\text{M}}^{\text{d}}], \%$$

where: A^{d} is the content of ash, %; $(CO_2)_{\text{M}}^{\text{d}}$ is the content of mineral carbon dioxide, %, both in dry bases.

The samples of coal differ in the content of total sulphur (from 1.01 to 7.04%) as well as in the content of different forms of sulphur and in the content of their mineral part. In the EOS sample the content of total sulphur was 1.63% and in its semicoke 2.2%. The content of organic matter in coal was between 87.2–91.7%, in EOS 33.2% and in its semicoke 17.7% (Table 1).

Methods

The experiments were carried out with thermogravimetric equipment (Q-Derivatograph, MOM; LabsysTM TG/DTA/DTC, Setaram) in dynamic heating conditions (5 K min⁻¹) in a stream of dry air up to 900°C, with absorption of the evolved gases

Table 1 Characteristics of fuels (dry basis)

Sample	Organic matter/%	Content/%						
		(CO ₂) _M	CaCO ₃	FeS ₂	Spyr	Ssulph	Sorg	Total
Coal-1	91.7	1.27	2.9	0.86	0.46	0.13	0.42	1.01
Coal-2	89.9	1.50	3.4	0.42	0.22	2.58	4.24	7.04
Coal-3	90.3	0	0	0	0	0.66	2.63	3.29
Coal-4	87.2	0.12	0.3	0.02	0.01	0.18	2.29	2.48
Oil shale	32.0	19.75	44.9	2.24	1.20	0.10	0.33	1.63
Semicoke	17.7	18.13	41.1	2.55	1.36	0.44	0.40	2.20

and titration of the solution at pH=4.0 [9, 10]. That enabled simultaneous fixation of TG, DTG, DTA, TGT and DTGT curves. Multiplate Pt-crucibles were used, the mass of the samples was 275–325 mg (by using LabsysTM: 15–20 mg). In the solid residue the content of sulphur was determined, some of the samples were subjected to X-ray diffraction and BET specific surface area analyses.

For modelling the CFBC process, the impact of EOS ash addition on the dynamics of SO₂ emission was studied. The mole ratio of free CaO/S varied from 1.0 to 3.0 and was regulated by the amount of oil shale ash formed during experimental combustion of EOS at 600–850°C in the bubbling fluidized bed boiler. The content of the total CaO and the free CaO in the ash was 66.2 and 46.4%, respectively.

Results and discussion

The behaviour of coal, EOS, its semicoke and their mixtures varied considerably at thermal treatment. For example, thermooxidation of coal-3 took place in the temperature interval from 280 to 600°C with exoeffects, accompanied by mass losses with maximums in DTA curve at 340 and 440 and a shoulder at 480°C, which correspond to thermooxidation of different parts of organic matter in coal. Up to 600°C, the mass loss was 90.8% of the total mass of the sample. The emission of SO₂ started at 280 and lasted up to 600°C, with maximums in the DTGT curve at 320, 380, 420 and a shoulder at 460°C, during which 69.8% of the total content of sulphur evolved (Fig. 1). As the sulphates contained in the fuels studied do not decompose until 900°C and coal-3 contains no pyritic sulphur, the amount of the emitted SO₂ was in accordance with the emission of 87.3% of organic or emittable sulphur.

Thermooxidation of EOS started at 250 and continued up to 540°C with two intensive exoeffects, accompanied by mass losses with maximums in the DTA curve at 340 and 460°C (Fig. 2). The first exoeffect corresponds to thermooxidation of the lighter part of volatile matter, the second one to thermooxidation of the heavier part

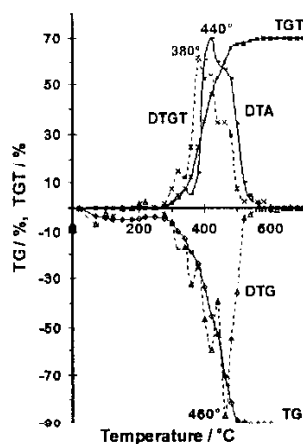


Fig. 1 Thermooxidation curves of coal-3. $m=287.2$ mg 5 K per min in the flow of air plate crucibles

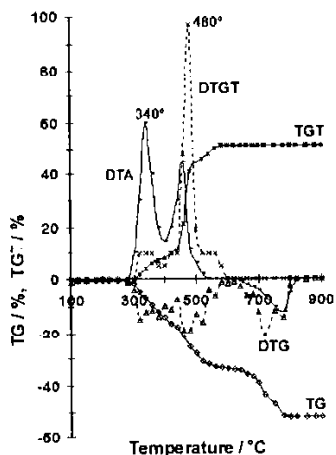


Fig. 2 Thermoanalytical curves of Estonian oil shale. $m=283.4$ mg 5 K per min in the flow of air plate crucibles

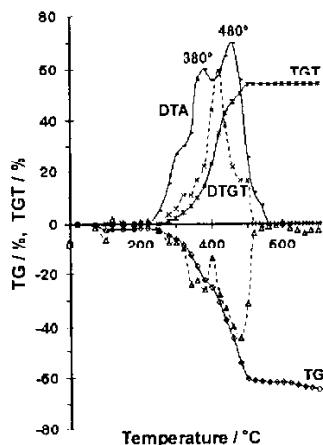


Fig. 3 Thermoanalytical curves of coal-3 and Estonian oil shale mixture (mass ratio 1:1). $m=288.5$ mg 5 K per min in the flow of air plate crucibles

of organic matter and pyrite. The endoeffect with a minimum in the DTA curve at 780°C correspond to the decomposition of carbonates in the mineral part of oil shale. The total mass loss up to 560°C was 30.7%, up to 850°C 51.7%. Emission of SO_2 in EOS started at 280°C and proceeded with maximums in the DTGT curve at 340 and 480°C and with low shoulders at 420 and 540, up to 600°C. Up to 51.5% of the total or 54.9% of the emittable sulphur evolved. SO_2 emission at the temperature interval of 280 to 340°C originates from the destruction of the lighter part of organic matter, of 340 to 520°C from the destruction of the heavier part of organic matter and pyrite.

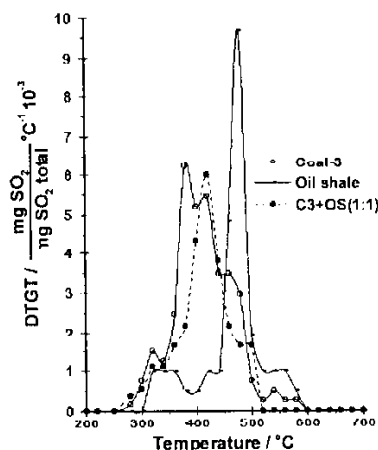
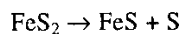


Fig. 4 DTGT curves of coal-3, EOS and their mixture (mass ratio 1:1)

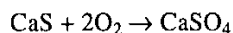
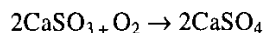
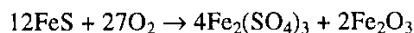
At the experiment of coal-3 and EOS mixture two intensive maximums in the DTA curve at 380 and 460°C and a shoulder at 320°C were observed (Fig. 3). The mass loss up to 560° was 64.1%, up to 850°C 70.5% of the total mass of sample. The emission of SO₂ took place with a very intensive maximum in DTGT curve at 420°C (shoulders at 320 and 480°C) and practically stopped abruptly at 520°C, i.e. at the temperatures where the decomposition of carbonates started in our experimental conditions. Up to 540°C, 53.4% of the total content of sulphur was emitted, or less than 7.2% was calculated for the mechanical mixture of coal-3 and EOS. The effect of the mixing of coal-3 and EOS on the dynamics of SO₂ emission is clearly shown in Fig. 4.

Thermooxidation of semicoke as well as of EOS took place with two exoeffects with maximums in DTA curve at 340 and 460°C and with an endoeffect with the minimum in DTA curve at 760°C, but the mass loss up to 540°C was 18.5% and up to 850°C 32.5% of the total mass of sample. Notable differences in the dynamics of SO₂ evolution into the gas phase compared with that of EOS were observed; the emission of SO₂ proceeded at a temperature interval from 280 to 600°C with a constant SO₂ emission rate, and up to 600°C only 10.1% of the total content of sulphur evolved (Fig. 6A). The emission of SO₂ during thermooxidation of coal-3 and semicoke mixture started at 280°C and lasted up to 560°C, the amount of the emitted SO₂ was limited to 36.9% of the total sulphur.

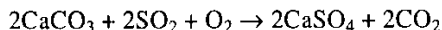
Considering the results of TG and X-ray diffraction analyses, the following transformations during thermal processing of EOS in reducing conditions at temperatures 550–600°C (i.e. during formation of semicoke) with pyritic sulphur take place:



which have a great influence on sulphur binding process in the following thermooxidative treatment of semicoke and its mixtures with the other fossil fuels. In oxidizing conditions the following transformations are possible:



and after the oxidation of sulphur to SO_2 :



The mixing of coal with EOS or its semicoke, but particularly the addition of oil shale ash, has a notable influence on the dynamics of emission as well as on the amount of the evolved SO_2 , which is well demonstrated in Figs 5 and 6. In the case of ash addition the emission of SO_2 also started at 200–300°C, but the emission stopped abruptly at 460–540, not at 580–620°C, like it was when ash was not added. The amount of SO_2 evolved into the gas phase decreased from 35–75% for the sample without oil shale ash addition to 7–30% for the samples with addition of ash, depending on the particular sample and on the mole ratio of free CaO/S in the mixture.

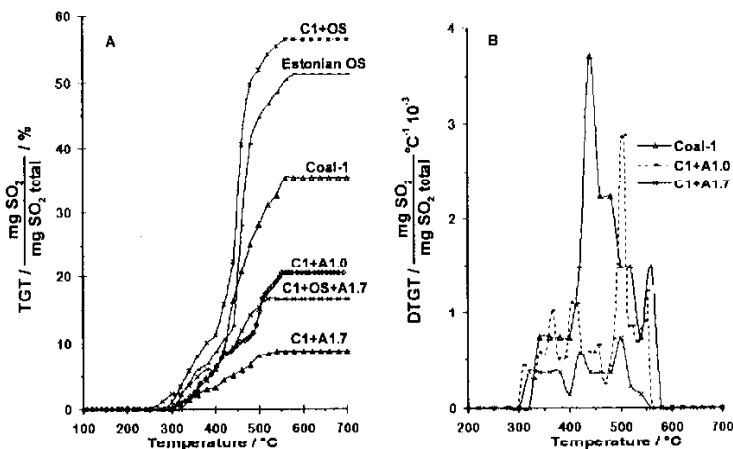


Fig. 5 TGT (5A) and DTGT (5B) curves for coal-1 (C1), EOS (OS) and their mixtures with and without oil shale ash addition (A) at mole ratio of free $\text{CaO/S} = 1.0$ or 1.7

Using the mixtures of EOS with coal in which sulphur is present mainly in pyritic form, the amount of the sulphur evolved exceeded that emitted during the thermooxidation of the sample of coal separately. For example, during thermooxidation of coal-1, in which 45.5% of the total sulphur was present in pyritic form, the emission of SO_2 started at 320 and lasted up to 560°C, where 35.8% of the total sulphur

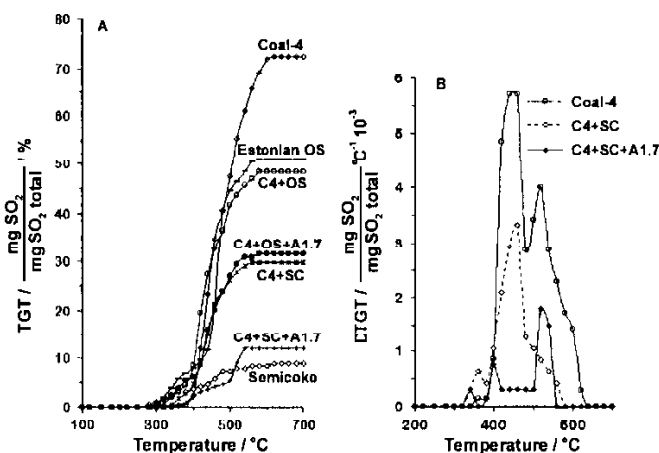


Fig. 6 TGT (6A) and DTGT (6B) curves for coal-4 (C4), EOS (OS), its semicoke (SC) and their mixtures with and without oil shale ash addition (A) at mole ratio of free $\text{CaO/S}=1.7$

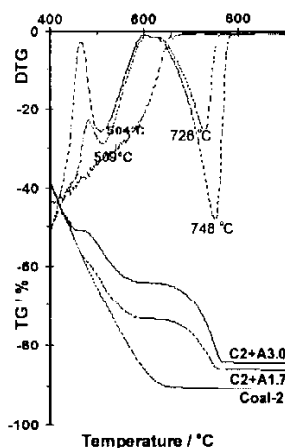


Fig. 7 TG and DTG curves for coal-2 (C2) with and without oil shale ash (A) addition at mole ratio of free $\text{CaO/S}=1.7$ and 3.0

evolved. For coal-1 and EOS mixture the temperature interval was 280 to 540 $^{\circ}\text{C}$ and 57.4% of the total sulphur evolved. This was caused by the cumulation of the effects of thermooxidation of pyrite in coal-1 and EOS in a quite narrow temperature range 440–480 $^{\circ}\text{C}$ (Fig. 5A). In coal-1, with ash addition, the emission of SO_2 took part at the same temperature interval, but reaching the mole ratio 1.0 and 1.7 of free CaO/S in the mixture, 20.5 and 9.1% of the total content of sulphur, respectively, evolved

(Fig. 5B). In the case of addition of oil shale ash (mole ratio of free CaO/S=1.7) into the coal and EOS mixture, 16.7% of the total sulphur was emitted.

Using the mixtures of EOS and its semicoke with coal, in which sulphur is present mostly in the form of organic sulphur, the influence of the carbonate part contained in oil shale and its semicoke prevailed in the SO₂ binding process – much more sulphur was bound in the solid phase than might be expected by the calculations. In Fig. 6 the influence of the mixing of oil shale and semicoke with coal-4 and the addition of oil shale ash on the emission of SO₂ is presented.

Another interesting effect in TG, DTG and DTA curves was observed when comparing those of the fuels with and without oil shale ash addition. For example, for coal-2 with addition of ash at mole ratio of free CaO/S=1.7 and 3.0 an endoeffect in DTA curves with minimums at 736 and 758°C was fixed, accompanied by mass losses with minimums in DTG curves at 726 and 748°C, respectively. This endoeffect corresponds to decomposition of secondary carbonates originated in free Ca, Mg-oxides formed in oil shale ash, during thermooxidation of organic matter of fuel at temperatures below 500–550°C. The additional mass loss of 14.3 and 19.9% followed the decomposition of secondary carbonates in coal-2 with addition of ash at mole ratio of free CaO/S=1.7 and 3.0, respectively (Fig. 7).

Conclusions

1. The dynamics of the emission of sulphur dioxide at thermooxidation of different samples of coal, EOS, its semicoke and their mixtures with mass ratio 1:1 and the influence of oil shale ash addition on the dynamics in dynamic heating conditions was studied. It was established that the dynamics of SO₂ emission depends on the form of sulphur (pyritic, organic, sulphate) and the content and composition of the mineral part of fuels and their mixtures.

By mixing EOS (74% of sulphur in pyritic form) and coal in which the pyritic form of sulphur also prevailed, the cumulation of emission of SO₂ was accompanied by the exoeffect of oxidation of pyrite.

The mixing of EOS with coal in which organic sulphur prevailed decreased the emission of SO₂ into the gaseous phase, due to the beginning of the formation of free Ca, Mg-oxides above 500–550°C, actively taking part in SO₂ binding.

The positive influence of semicoke and its mixtures with the other studied fuels on the binding of SO₂ during thermooxidation is caused by the transformations in the organic and mineral part of EOS during its thermal processing in reducing conditions up to 550–600°C.

2. The addition of oil shale ash has a notable influence on the dynamics and on the amount of the SO₂ liberated. SO₂ emission from the fuels with addition of ash started approximately at the same temperatures as for fuels without the addition, but stopped quite abruptly at 460–520°C, not at 550–650°C. Depending on the composition of a coal sample and on the mole ratio of free CaO/S in the fuel – ash mixtures, the amount of the SO₂ evolved decreased from 35–75% without the addition of ash to 7–30% with ash addition.

In addition to SO₂, a part of the CO₂ formed during thermooxidation of organic matter of fuels was bound in the solid phase; the secondary carbonates formed decomposed at temperatures above 550–600°C.

3. The results of these investigations indicate the possibility of a significant reduction of SO₂ emission into the atmosphere by the combustion of sulphur-rich coal in the mixture with EOS, in particular, when using the circulating fluidized bed technique.

Utilization of semicoke of EOS by burning it in the mixtures of different solid fossil fuels makes it possible to eliminate a serious source of contamination of the environment with toxic compounds and to use the energy potential of semicoke.

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